Electrodeposited metallic thin films

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Thin films

- Nano-materials and nano-technology indebt greatly to thin film technology
- Three types of nano-materials
  - Zero-dimensional (Quantum dots)
  - One-dimensional (Quantum wires)
  - Two-dimensional (Thin films)

Thin Films

- Thin films are two dimensional structures, having sizes more or less 1000 Å.
- Features different from bulk materials.
  - Mechanical strength, carrier transportation, superconductivity, ferroelectricity, magnetic and optical properties.

Why we need thin films

- Rapid development of miniaturization.
- Surface coatings and decorative
- Components become wear tear resistive.
- Hard disc drives
- Automotive parts
- Electrical contacts
- Engineering components
- Gold-silver ware and jewelry
- Musical instruments and trophies
- Micro parts for MEMS
- …and many more

Advantageous features

- The science of thin film has helped us in,
  - Developing new materials.
  - Tailoring of interface – surfaces
  - Improved chemical stability
  - New processing techniques
  - Tailoring of microstructure
  - New physical properties
  - New patterning techniques
  - In-situ characterization

Thin film growth process

- **Any thin film growth process involves three main steps.**
  - Production of appropriate atomic, molecular or ionic species
  - Transport of these species to the substrate through appropriate medium
  - Condensation on substrate, either directly or via a chemical and/or electrochemical reaction to form a solid deposit.

Thin film preparation techniques

- Depositing atoms on to a substrate
- Variety of methods are available
  - Chemical vapor deposition (CVD)
    - Electrodeposition
    - Plasma CVD
    - Laser CVD
    - Chemical solvent
  - Physical vapor deposition (PVD)
    - Thermal evaporation
    - Pulsed laser deposition (PLD)
    - Molecular beam epitaxy (MBE)
    - Ion implanting
    - Sputtering

Electro deposition

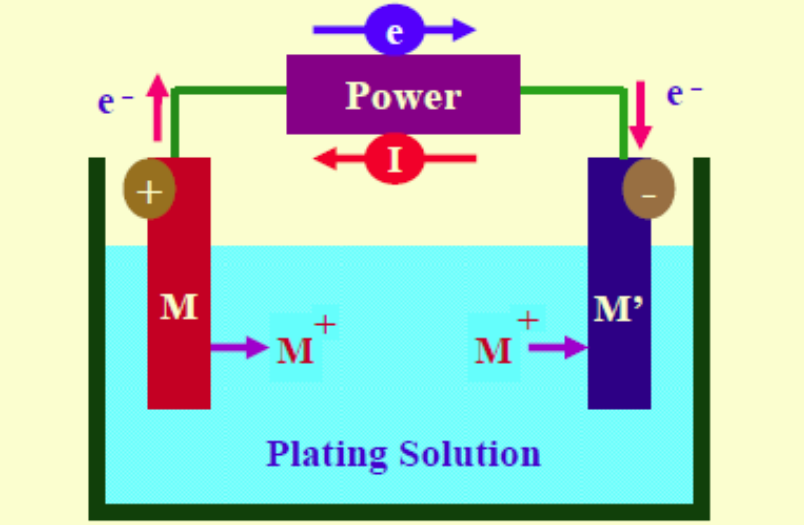
- Electro deposition is the process of coating a thin layer of one metal on top of a different metal or substrate, using a very small electric potential, to modify its surface properties.
  - The cations of a desired material/metal achieved from an electrolytic solution are reduced and subsequently deposited on to a conducting surface called substrate.
  - The electrolytic solution contains positively (cations) and negatively (anions) charged ions. Under the application of external electric field, the cations migrate to cathode, discharged and deposited.
  - $Ni^{2+} + 2e \rightleftarrows Ni$ (metal) at cathode
  - $Ni \rightleftarrows Ni^{2+} + 2e$ at anode

Faraday's law

- The amount of electrochemical reaction that occurs at an electrode is proportional to the quantity of electric charge (Q) that passes through the cell.
  - If the weight of the product of electrolysis is W, then W = ZIt, where Q = It and Z is electro chemical equivalent (Z = 96478.462 C)
  - The production of 1 gram equivalent of a product at the electrode in a cell needs 96478.462 Coulombs.

Electrodeposition

- The chemical reaction around the electrode area is not as simple as it seems to be. Under the influence of an applied potential, rearrangement of ions near the electrode surface results in an electrical double layer called the Helmholtz double layer, followed by the formation of a diffusion layer. These two layers are referred as the Gouy-Chapman layer.
- Migration
- Electron transfer
- Neutralization
- Adsorption



Factors influencing electrodeposition

- The morphology and composition of elect-rodeposits vary significantly and depends on:
  - Current density
  - Nature of anions or cations in the solution
  - Bath composition and temperature
  - Solution concentration
  - The presence of impurities
  - Physical and chemical nature of the substrate surface
    - Substrate cleaning

Electrochemical Series

- A series in which metals are listed in the order of their chemical reactivity.
- K is stronger than Mg, so if K is heated with $MgNO_3$, it react s immediately to form KNO_3 and Mg.

Reaction (Oxidised form + ne⁻ → Reduced form)	$E^\ominus$/V
$F_2(g) + 2e^- \rightarrow 2F^-$	2.87
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.81
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51
$Au^{3+} + 3e^- \rightarrow Au(s)$	1.40
$Cl_2(g) + 2e^- \rightarrow 2Cl^-$	1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33
$O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23
$MnO_2(s) + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.23
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09
$NO_3^- + 4H^+ + 3e^- \rightarrow NO(g) + 2H_2O$	0.97
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.92
$Ag^+ + e^- \rightarrow Ag(s)$	0.80
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77
$O_2(g) + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68
$I_2 + 2e^- \rightarrow 2I^-$	0.54
$Cu^+ + e^- \rightarrow Cu(s)$	0.52
$Cu^{2+} + 2e^- \rightarrow Cu(s)$	0.34
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$	0.22
$AgBr(s) + e^- \rightarrow Ag(s) + Br^-$	0.10
$2H^+ + 2e^- \rightarrow H_2(g)$	0.00
$Pb^{2+} + 2e^- \rightarrow Pb(s)$	-0.13
$Sn^{2+} + 2e^- \rightarrow Sn(s)$	-0.14
$Ni^{2+} + 2e^- \rightarrow Ni(s)$	-0.25
$Fe^{2+} + 2e^- \rightarrow Fe(s)$	-0.44
$Cr^{3+} + 3e^- \rightarrow Cr(s)$	-0.74
$Zn^{2+} + 2e^- \rightarrow Zn(s)$	-0.76
$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	-0.83
$Al^{3+} + 3e^- \rightarrow Al(s)$	-1.66
$Mg^{2+} + 2e^- \rightarrow Mg(s)$	-2.36
$Na^+ + e^- \rightarrow Na(s)$	-2.71
$Ca^{2+} + 2e^- \rightarrow Ca(s)$	-2.87
$K^+ + e^- \rightarrow K(s)$	-2.93
$Li^+ + e^- \rightarrow Li(s)$	-3.05

Increasing strength of oxidising agent ↑

Increasing strength of reducing agent ↓

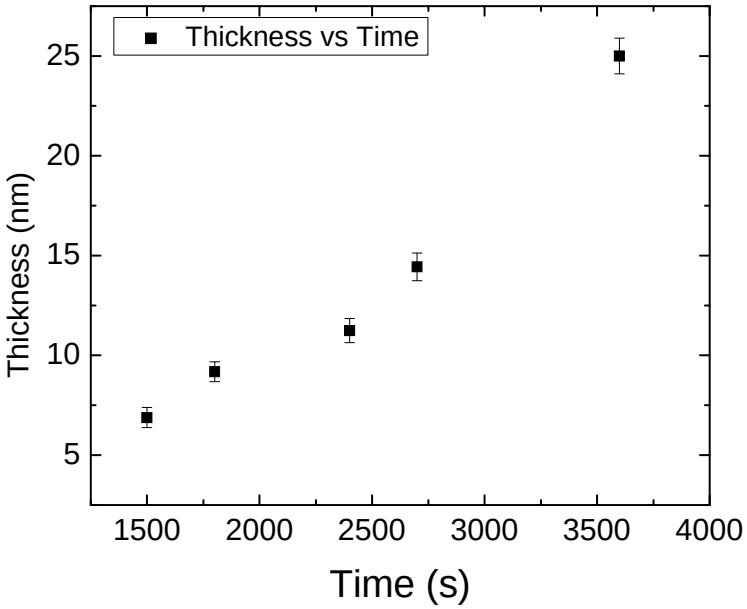
Typical compositions for Ni and Cu deposition

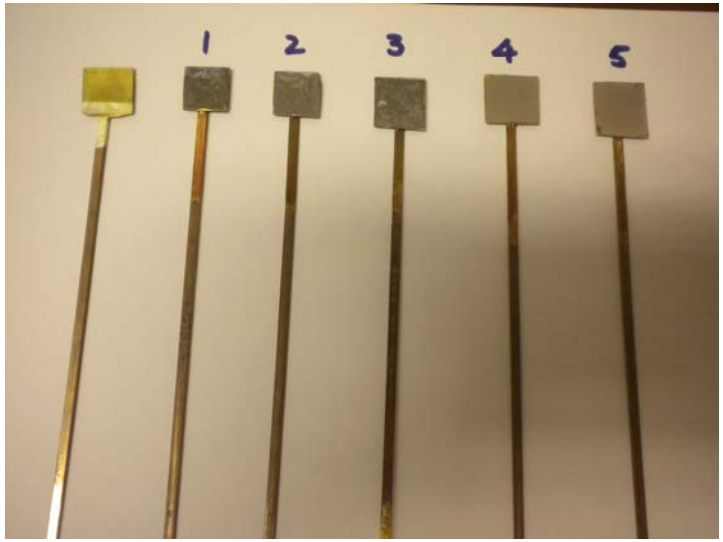
- For Ni films
  - Nickel sulphate ….90 g per litre
  - Nickel chloride ….200 g per litre
  - Boric acid …….40 g per litre
  - Cathode ..99% pure brass
  - Anode ….99% pure Ni tablet
  - Optimum temp. ~ 70 ˚C
  - p_H ~ 4
- For Cu films
  - Copper sulphate ….100 g per litre
  - Sulfuric acid ……..17.5 ml per litre
  - Cathode ….99% pure stainless steel
  - Anode …..99% pure Cu

Results

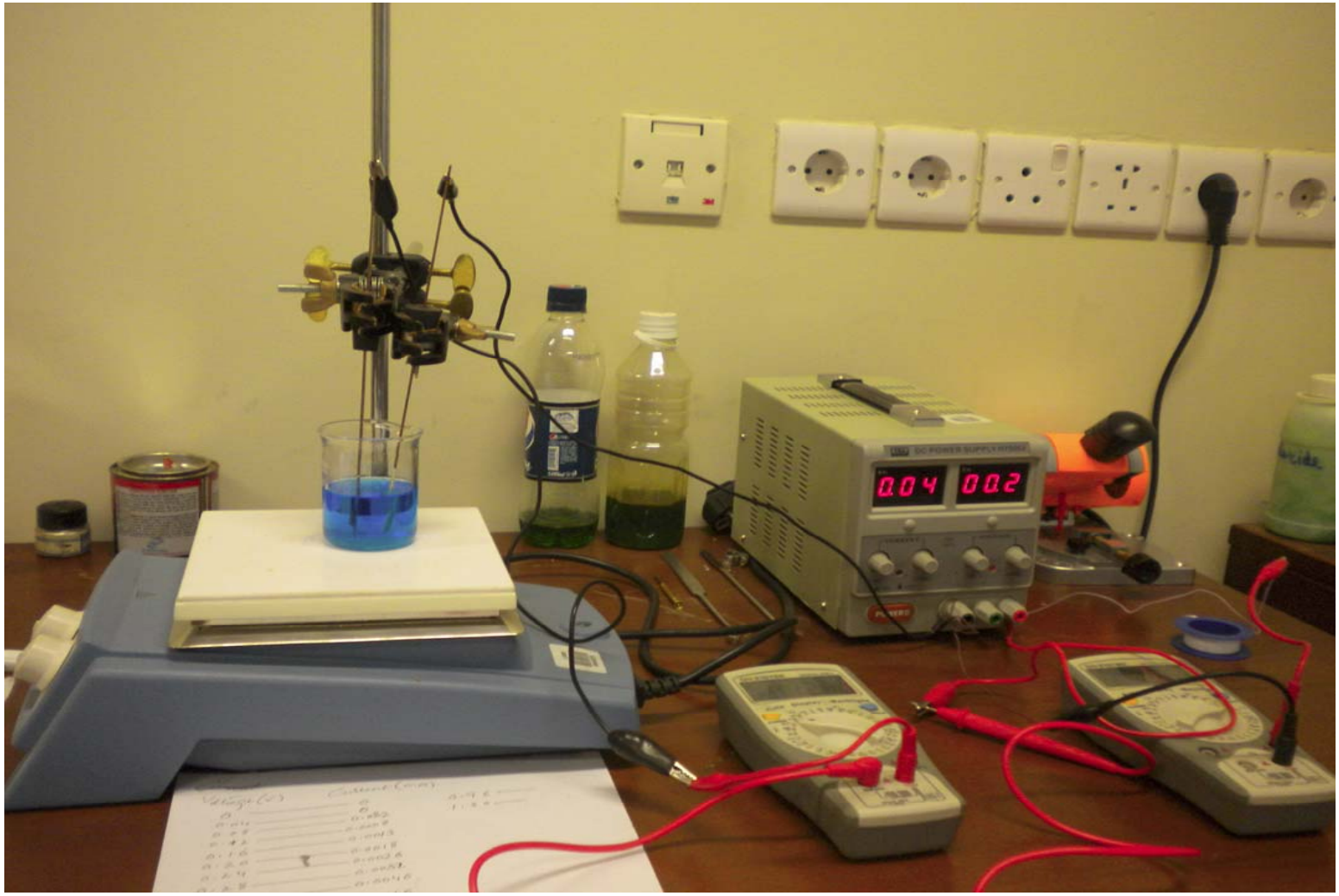
Sample #	Area of Substrate (cm^2)	Time (s)	Voltage (V)	Current I (mA)	Charge (C) Q=It	n(e) =Q/F	n(Ni)= 1/2n(e)	MM_{Ni} (g)	Thickness = $M_{Ni}/d.A$
1	3.5004	1500	0.8	0.047	0.0705	$7.3x10^{-7}$	$3.65 x10^{-7}$	$2.14 x10^{-5}$	6.88 nm
2	2.4764	1800	0.8	0.037	0.0666	$6.9x10^{-7}$	$3.45 x10^{-7}$	$2.03 x10^{-5}$	9.18 nm
3	2.5513	2400	0.8	0.035	0.0841	$8.7x10^{-7}$	$4.35 x10^{-7}$	$2.55 x10^{-5}$	11.24 nm
4	3.2577	2700	0.8	0.051	0.1377	$1.4x10^{-6}$	$7.0 x10^{-7}$	$4.188 x10^{-5}$	14.43 nm
5	3.2972	3600	0.8	0.067	0.2412	$2.5x10^{-6}$	$1.25 x10^{-6}$	$7.34 x10^{-5}$	25.00 nm

Results

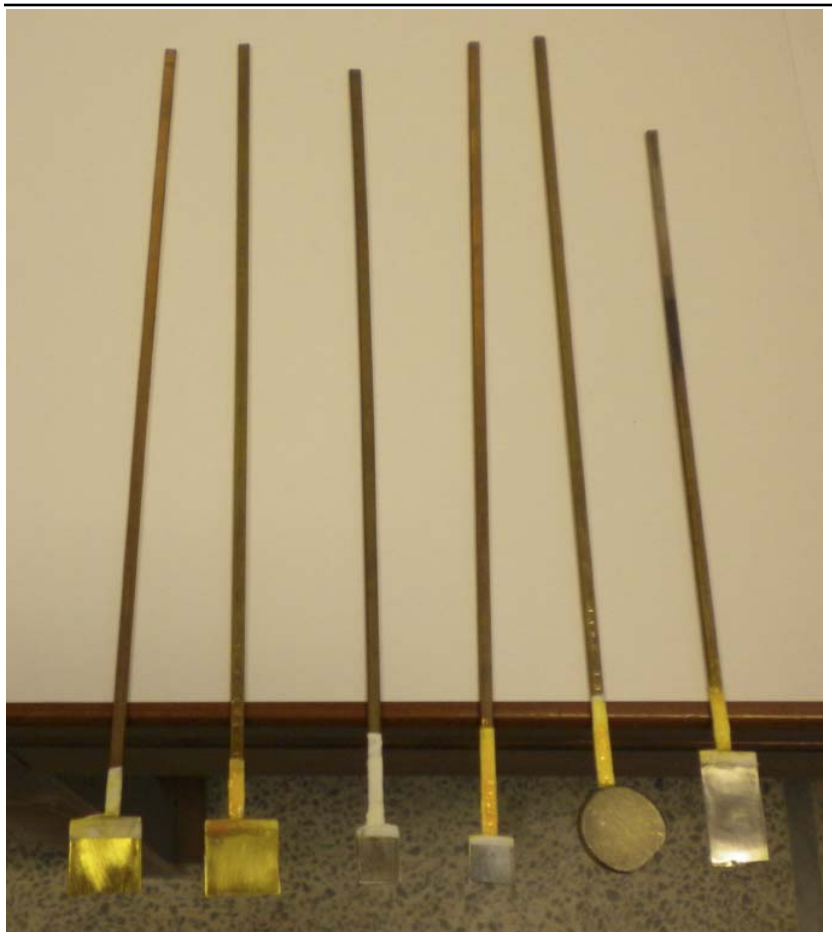

Thickness vs Time
Thickness (nm)
25
20
15
10
5
1500
2000
2500
3000
3500
4000
Time (s)

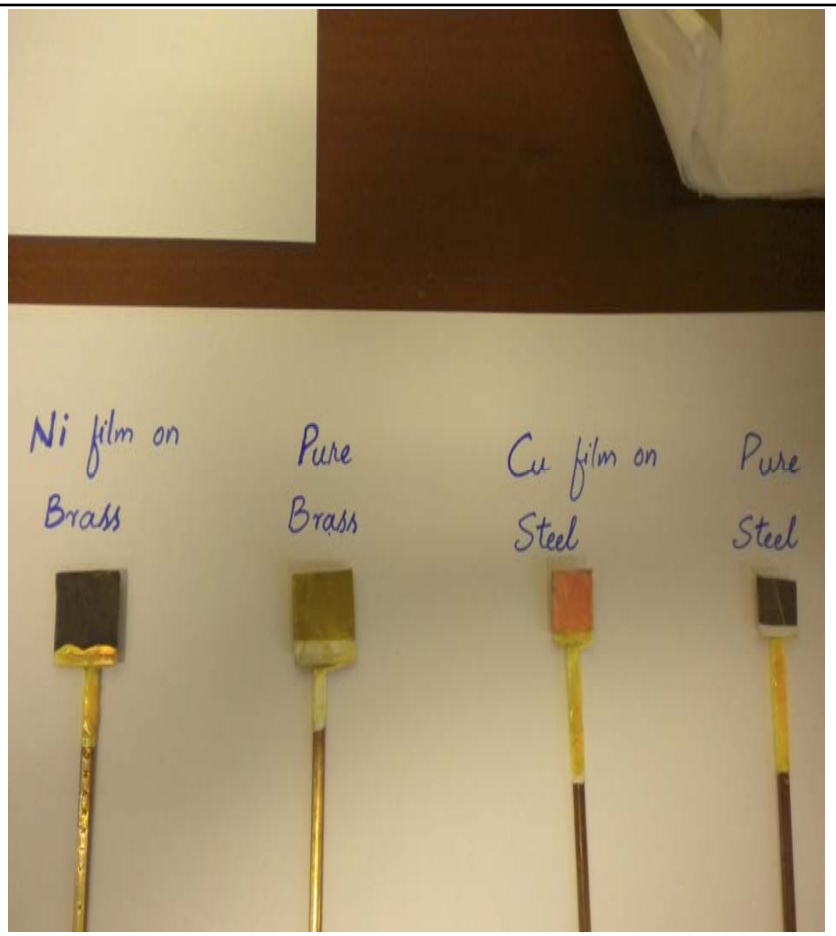

1
2
3
4
5

Experimental Set up



Deposited Metals and Substrates





Characterization Required

- Phase analysis with XRD.
- Composition analysis with XRF, EDX, MS, XPS, AES etc.
- Thickness with AFM, SEM, ellipsometry
- Surface roughness with AFM
- Surface morphology and structure with SEM, TEM

Future projects

- Growth of metallic thin films on non-conducting substrates, i.e. Glass, Si
- For this purpose,
  - A very thin conducting layer of ITO will be deposited
  - Nucleation centers will be grown by dipping the substrates into the solution of $PbCl_2$, $PdCl_2$, $SnCl_2$ or $H_2PtCl_6.6H_2O$

Thank you