Summer 6-26-2005

XII, Part 1: Novel properties of glass-metal nanocomposites

D Chakravorty
Indian Association for the Cultivation of Science

An IMI Video Reproduction of Invited Lectures from the 17th University Glass Conference

NOVEL PROPERTIES OF GLASS-METAL NANOCOMPOSITES

D.CHAKRAVORTY

Unit on Nano Science and Technology

Indian Association for the Cultivation of Science
Kolkata 700032,India

Acknowledgment:

S.Basu, P.K.Mukherjee, S.K.Saha, B.N.Pal, A.Dan, S.Bhattacharya, Supriya Chakraborty

Department of Science and Technology,New Delhi

Indian National Science Academy, New Delhi

OUTLINE

- Glass-Ceramics → Template for nano metal growth.
- Silver nanowires in gel derived silica glass → Single electron tunneling
- Silver nanowires in fluorophlogopite mica glass-ceramics → Giant dielectric permittivity
- Metal core-metal oxide shell nanostructure in silica glass → Interfacial amorphous phase
- Glass-Ceramic- metal nanocomposites → Large Relative Humidity Sensitivity
- Silicate glass with nano metal arrays → Diode- like behaviour

Growth of Nanocrystalline Metal at Glass-Crystal Interface

Glass $55SiO_2$ $12ZnO$ $32.2\ Li_2O$ $0.8P_2O_5$

↓

Heat treated

565^0C / 1 hr.+ 630^0C/3 hr.

↓

Glass- Crystal Composites

$Zn_2SiO_4 + Li_4P_2O_7$: Crystalline phase

↓

Ion Exchange

$Li^+ \leftrightharpoons Ag^+$(Silver Nitrate at 310^0C/8 hr.

$Li^+ \leftrightharpoons Cu^+$ (CuCl,510^0C/3 hr.)

$3Li^+ \leftrightharpoons Fe^{3+}$($FeCl_3$,$300^0C$/50 hr)

↓

Reducible ion enriched Glass-Crystal Composite Layer

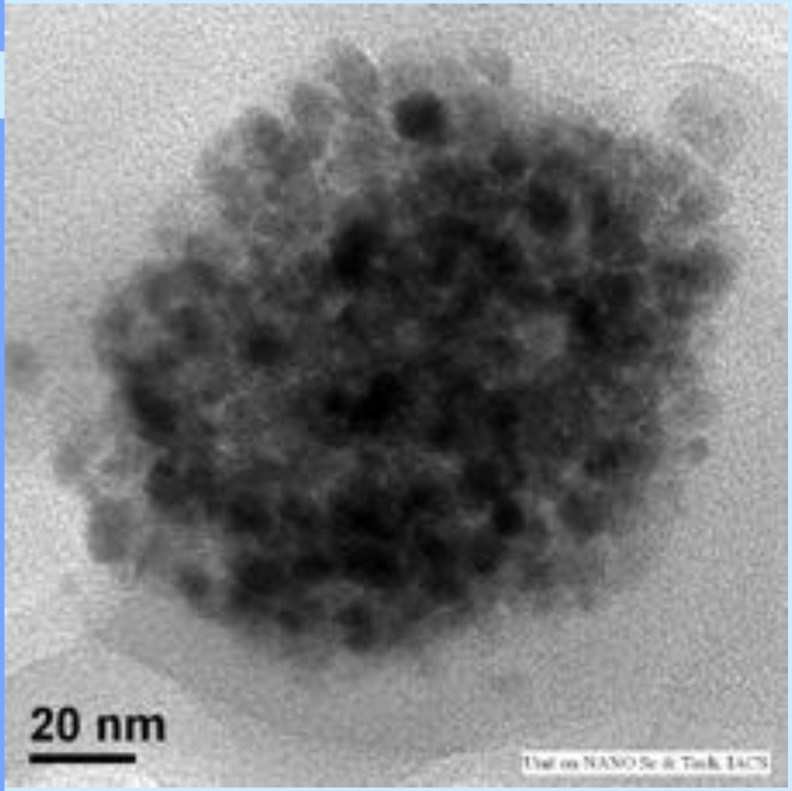
↓

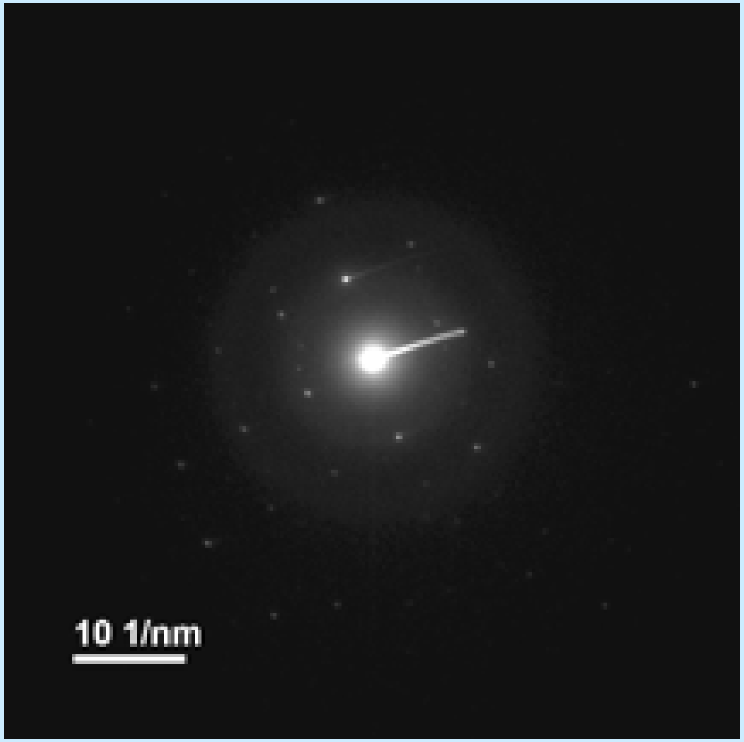
Reduction in H_2

↓

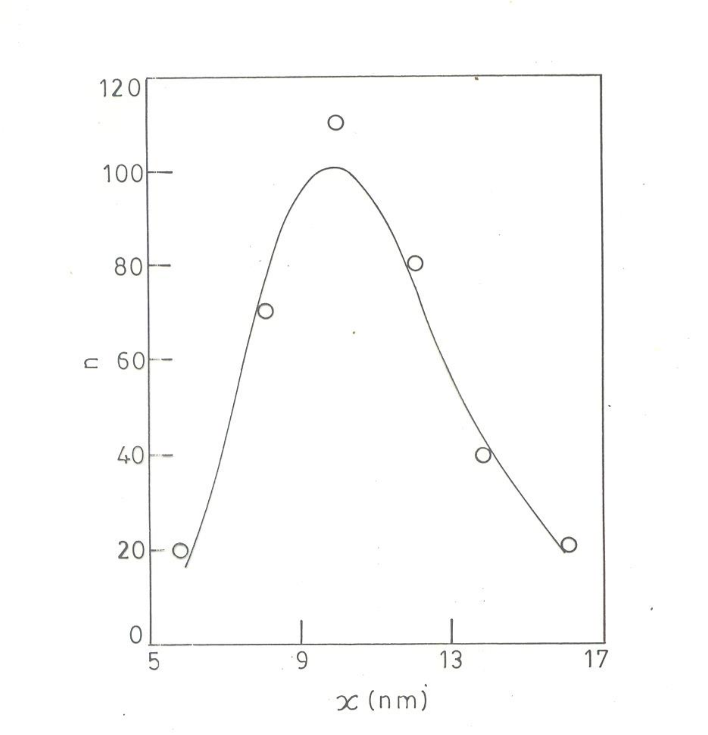
Nanoparticles of Metal at Glass-Crystal Interface

Growth of Nanocrystalline Metal at Glass-Crystal Interface





Growth of Nanocrystalline Metal at Glass-Crystal Interface

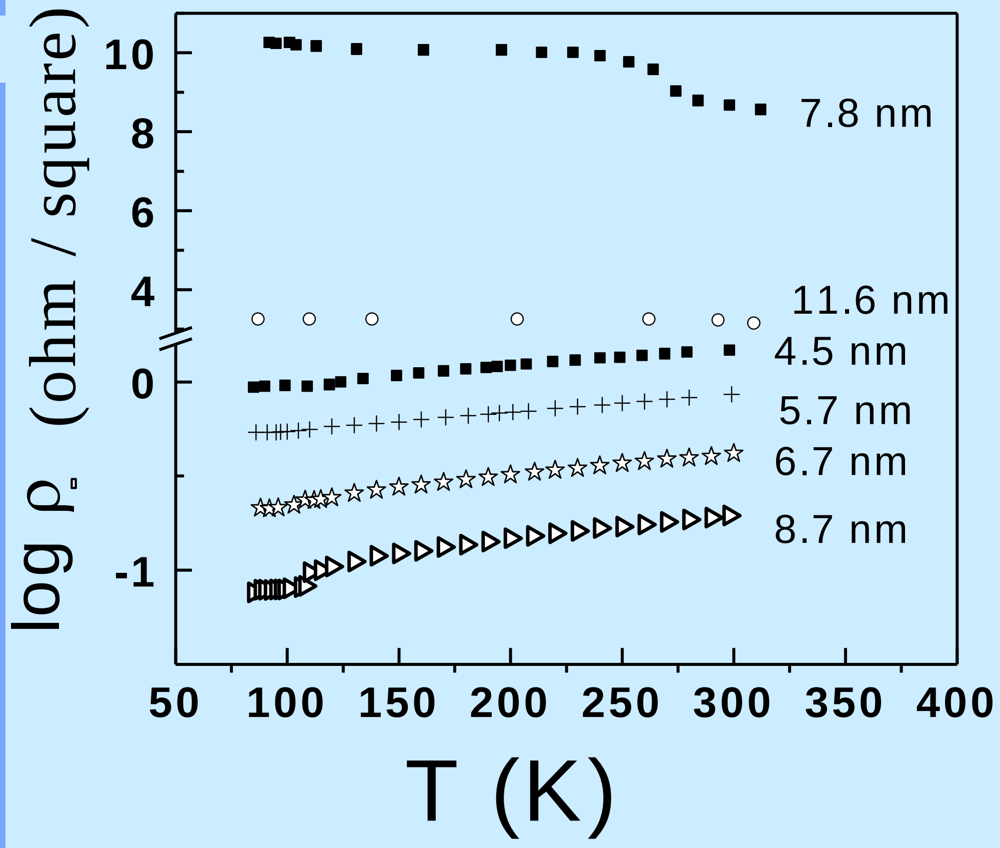


Size distribution of Silver Particles Synthesized by ion exchange and reduction(873K for ½ hr) in a glass of Composition

55SiO_2 ,32.2 LiO_2,12 ZnO,0.8P_2O_5

$$\Delta n = \frac{1}{\sqrt{2\pi} \cdot \ln \sigma} \exp\left\{ -\frac{1}{2} \left(\ln(\frac{x}{\bar{x}}) / \ln \sigma \right)^2 \right\} \Delta(\ln x)$$

Growth of Nanocrystalline Metal at Glass-Crystal Interface



Growth of Nanocrystalline Metal at Glass-Crystal Interface

Electron Tunnelling between Metal Islands

Neugebauer and Webb model:

$$\rho \propto \exp(2\alpha s + E/kT)$$

α : Tunnelling exponent $\left(= \left(\frac{2m\phi}{\hbar^2}\right)^{1/2} \right)$

s : Inter-Grain distance

E : Energy to charge a grain

ϕ : Effective barrier height

$$E = \frac{e^2}{2\pi\varepsilon\varepsilon_0}\left(\frac{1}{r} - \frac{1}{r+s}\right)$$ (Tick and Fehlner 1972)

e : electronic charge

r : metal grain radius

ε : dielectric constant of matrix

ε_0 : dielectric permittivity of free space

NANOWIRES IN SILICA GEL NANOPORES

GEL SAMPLES HEAT TREATED AT TEMPERATURES 523 TO 823 K FOR 6 HRS

↓

DIPPED INTO A SOLUTION OF $AgNO_3$

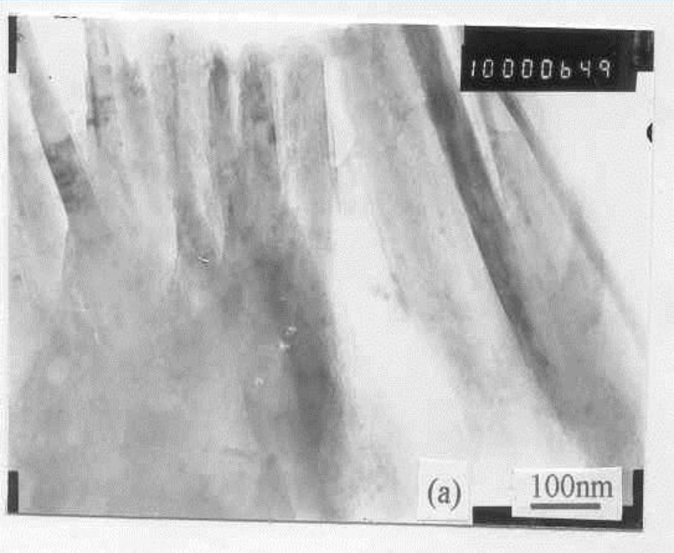
↓

SAMPLES COATED WITH SILVER PASTE ELECTRODES

↓

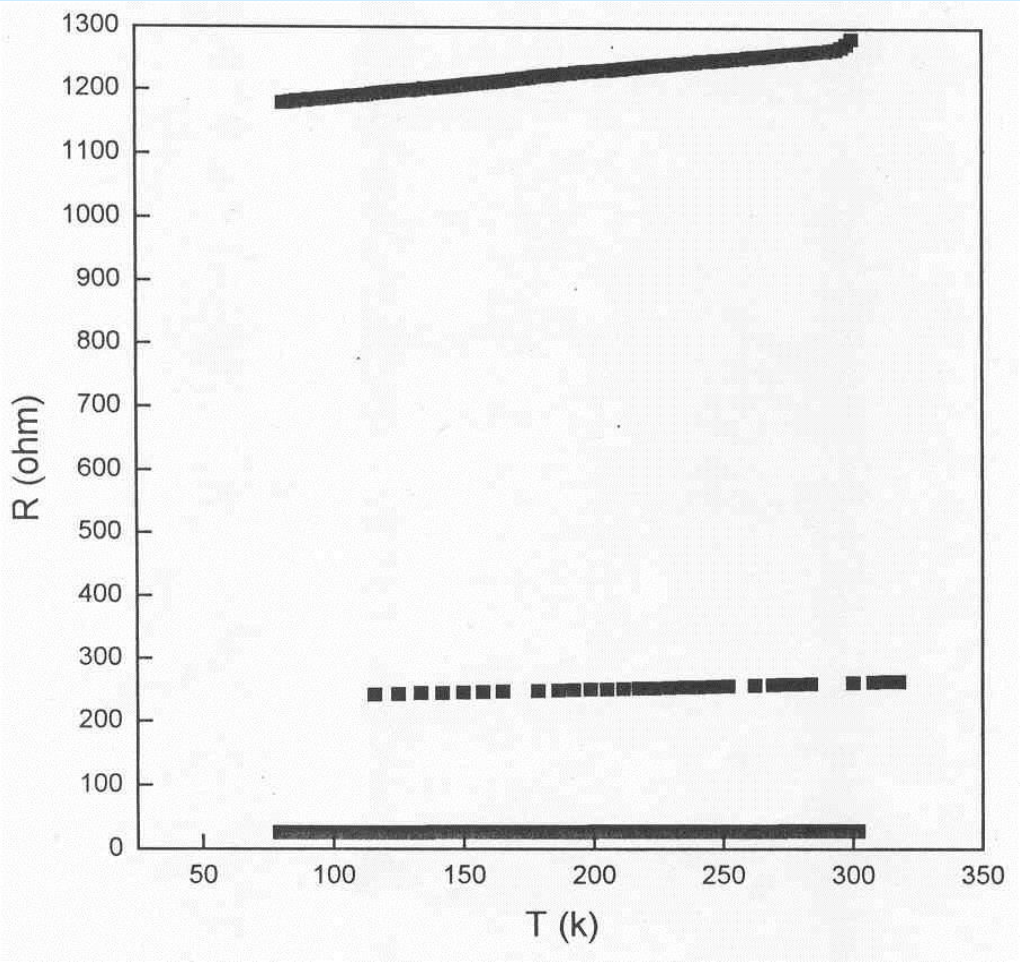
ELECTRODEPOSITION AT 8 VOLTS

SILVER NANOWIRES IN SILICA GEL

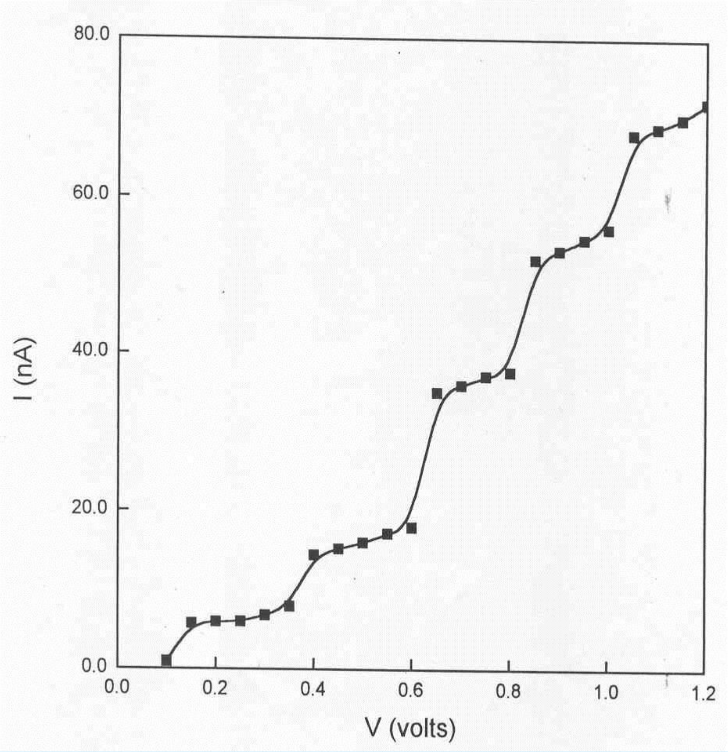


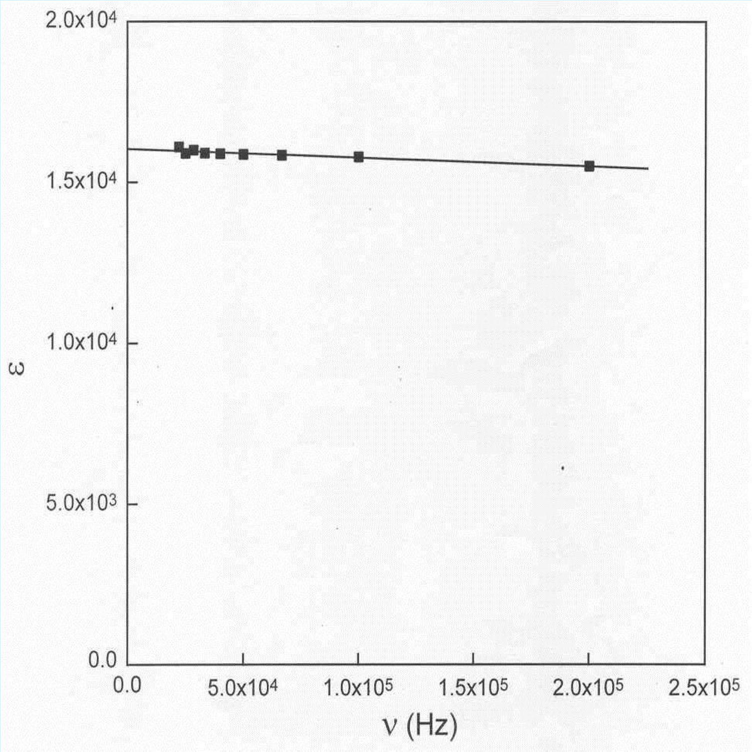
TEM for silica gel heat at 723K/6h.soaked AgNO3 and Subjected to electrodiposition

SILVER NANOWIRES IN SILICA GEL



SILVER NANOWIRES WITH BREAK JUNCTION IN SILICA GEL





BHATTACHARYYA et. al. Appl. Phys. Lett 77 3770 (2000)

GROWTH OF SILVER NANOWIRES IN NANO CHANNELS OF FLUOROPHLOGOPITE MICA ($KMg_3AlSi_3O_{10}F_2$)

GLASS COMPOSITION (TYPICAL) :

42 SiO_2 15 B_2O_3 9Al_2O_3 8 MgO 20 K_2O 6KF

↓

HEAT TREATMENT AT 1168 K FOR 2 HRS

↓

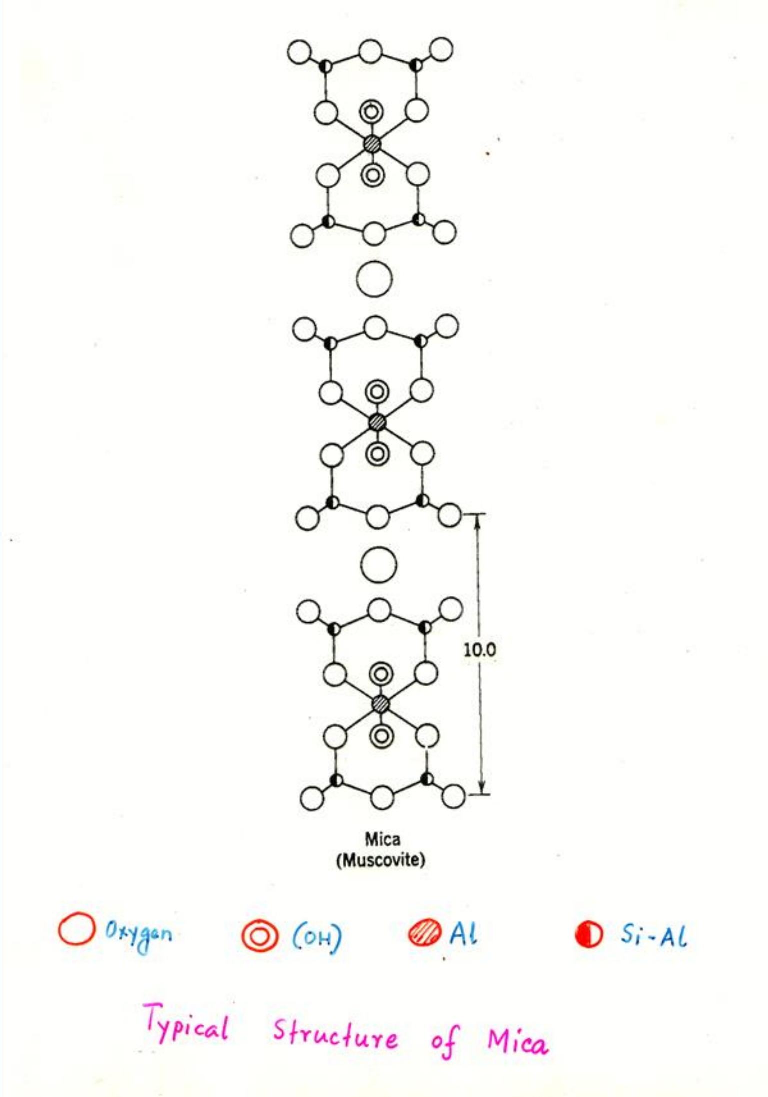
ION EXCHANGED IN $AgNO_3$ AT 573 K FOR 24 HRS

↓

ELECTRODEPOSITION WITH 10 VOLTS AT 370 K

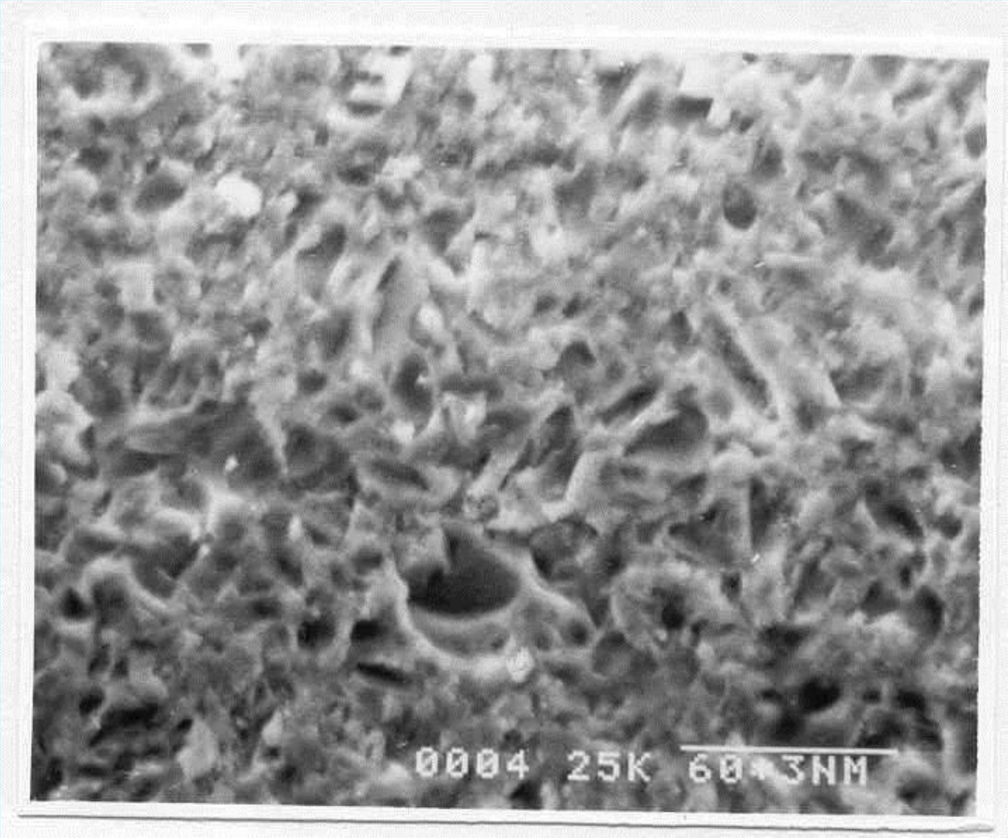
(SILVER PASTE ELECTRODES)

GROWTH OF SILVER NANOWIRES IN NANO CHANNELS OFFLUOROPHLOGOPITE MICA



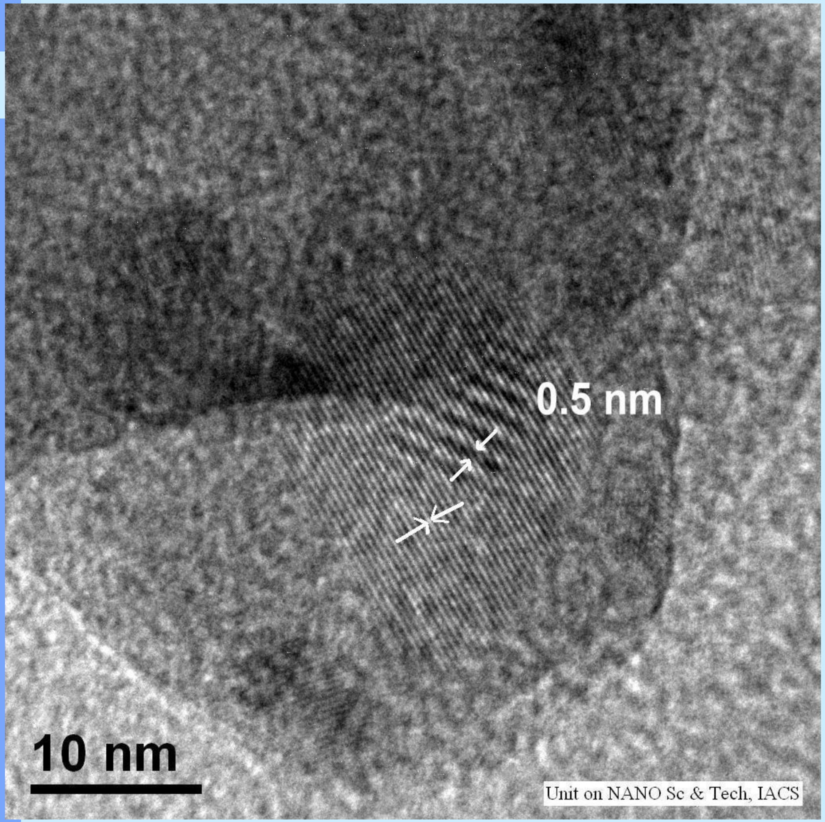
Crystal Channels as Templates for Growing Nanowires

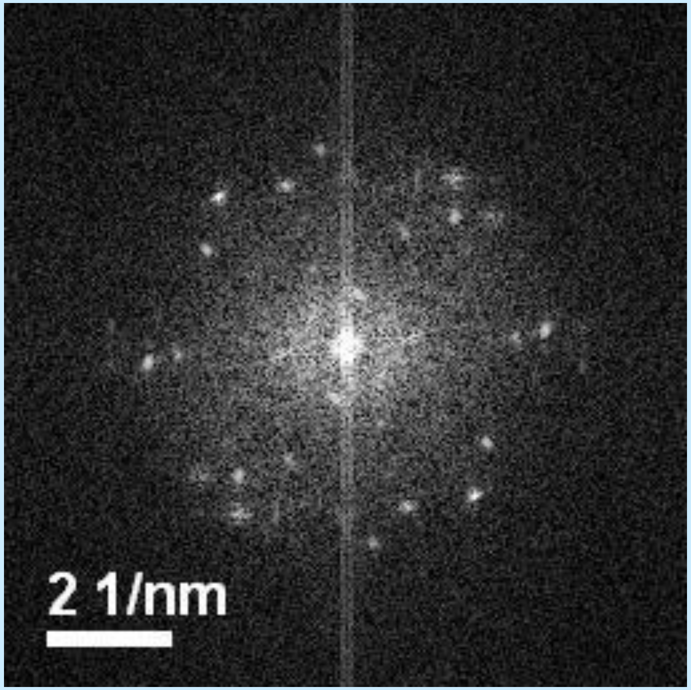
GLASS CERAMICS WITH FLUOROPHLOGOPITE MICA



SEM

NANOWIRES IN GLASS CERAMICS CONTAINING FLUOROPHLOGOPITE MICA



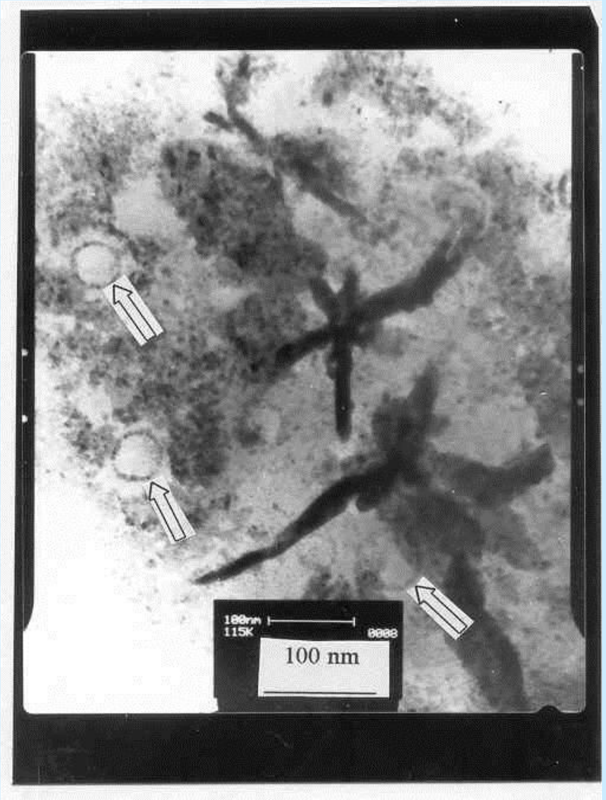


NANOWIRES IN GLASS CERAMICS CONTAINING FLUOROPHLOGOPITE MICA

Interplanar spacing d_{hkl} Specimen
heat treated at 1165 K / 2 hr +ion exchanged at 573 K / 24 hr

Experimental value Specimen heat treated at 1163K for 2 hr.and ion exchanged at 573 K for 24 hr. (nm)	Standard X-ray data for $K Mg_3 Al Si_3 O_{10} F_2$ (nm)
1.0769	0.996 (001)
0.4666	0.459 (020)
0.375	0.365 (112)
0.304	0.313 (112)
0.250	0.249 (131)

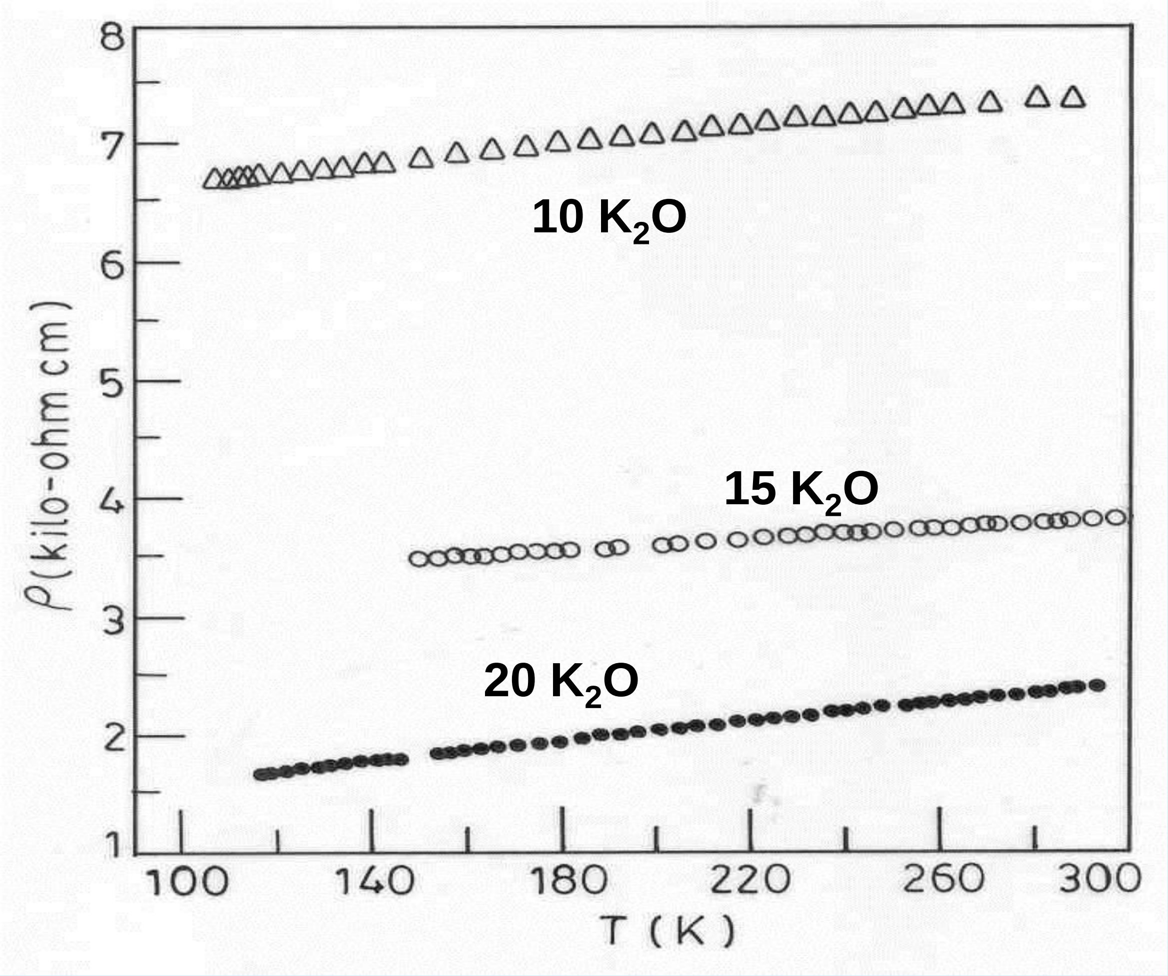
GROWTH OF SILVER NANO PARTICLES IN GLASS CERAMICS CONTAINING FLUORPHLOGOPITE MICA



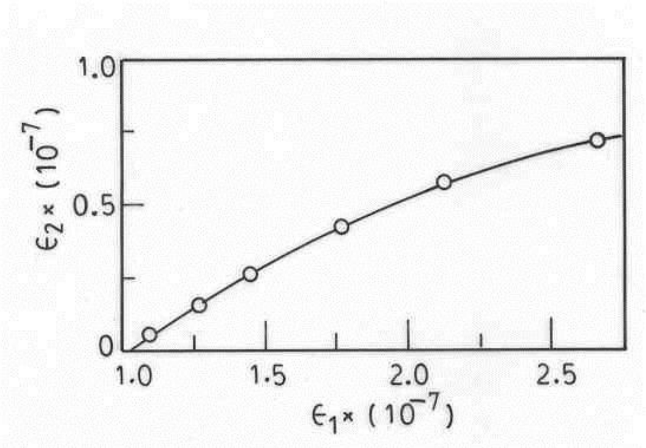
GLASS COMPOSITION

47 SiO_2 15 B_2O_3 12Al_2O_3 10 MgO 10 K_2O 6KF

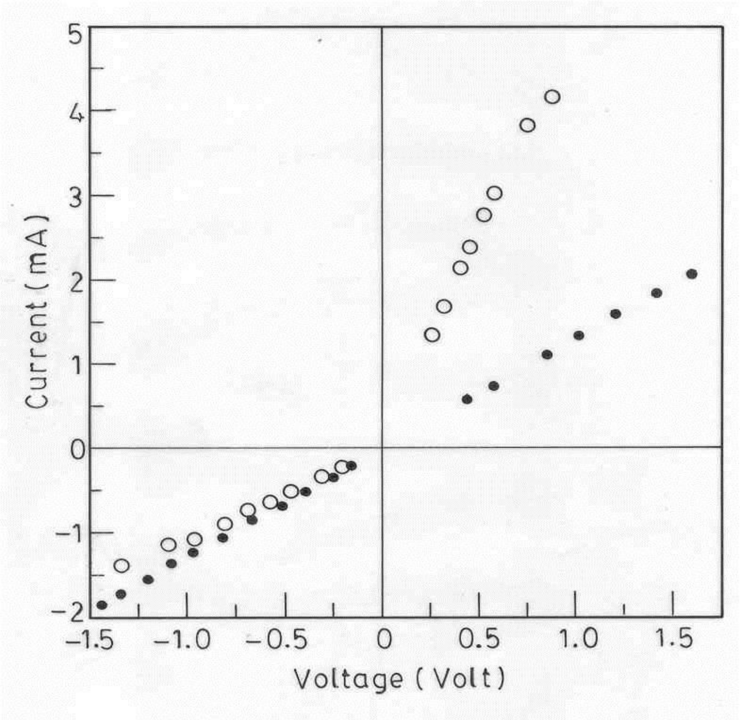
SILVER NANOWIRES IN GLASS CERAMICS CONTAINING FLUOROPHLOGOPITE MICA

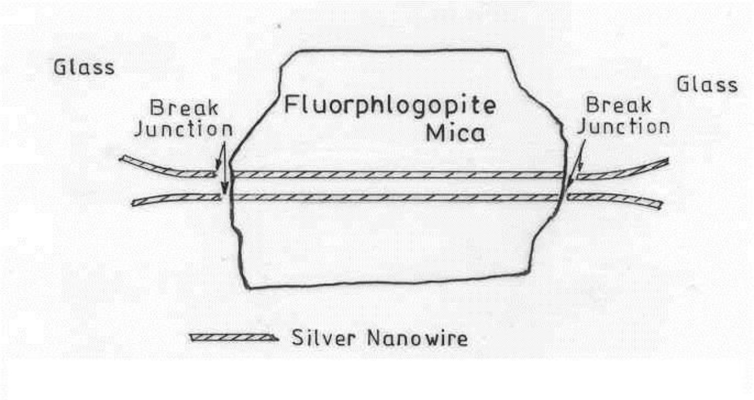


SILVER NANOWIRES IN GLASS CERAMICSCONTAINING FLUOROPHLOGOPITE MICA



COLE-COLE DIAGRAM





SCHEMATIC OF BREAK JUNCTIONS

MUKHERJEE AND CHAKRAVORTY J. Mater. Res., 17 3127 (2002)

SILVER NANOWIRES IN MICA CHANNELS– ULTRA HIGH DIELECTRIC PERMITTIVITY

SPACE CHARGE POLARIZATION MODEL FAILS TO EXPLAIN HIGH ε

MECHANISM IS ELECTRONIC

INTERRUPTED STRAND MODEL (RICE & BERNASCONI, 1972, PRL)

$$\varepsilon \cong 1/2(q_s l_o)^2$$

$\mathbf{l_0}$: STRAND LENGTH ; $\mathbf{l_0}$ = 1287 nm

$\mathbf{q_s}$: FERMI THOMAS SCREENING WAVE VECTOR OF CONDUCTION ELECTRONS

$\mathbf{q_s} \sim a^{-1}$ FOR METALLIC DENSITIES; FOR $\varepsilon \sim 10^7$ AND a = 0.28 nm

IN AGREEMENT WITH MICA CRYSTALLITE DIMENSIONS

COPPER CORE COPPER OXIDE SHELL – INTERFACIAL AMORPHOUS PHASE

Preparation :

Terget gel composition 60 CuO. 40 SiO_2 (mole%)

Precursors : ***$CuCl_2$. $2H_2O$, $Si(OC_2H_5)_4$***

Sol$^{\eta}$: ***60 ml C_2H_5OH, 10 ml dist H_2O, 1 ml HCL,125 ml Si $(OC_2H_5)_4$***

Reference Sample ← **Hot Pressed** ← **GEL**

↓ *REDCN 650^{o}C / 30 Min*

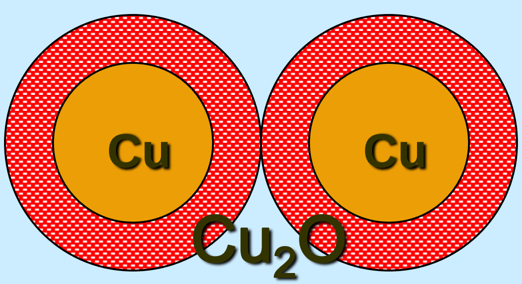
Sample (Metallic Conduction) ← **Hot Pressed** ← **Nanosized Metal (Cu)** (ξ=6.8 nm)

↓ *OXDN 450^{o}C - 850^{o}C / 30 Min*

Cu_2O (CuO) coated Cu

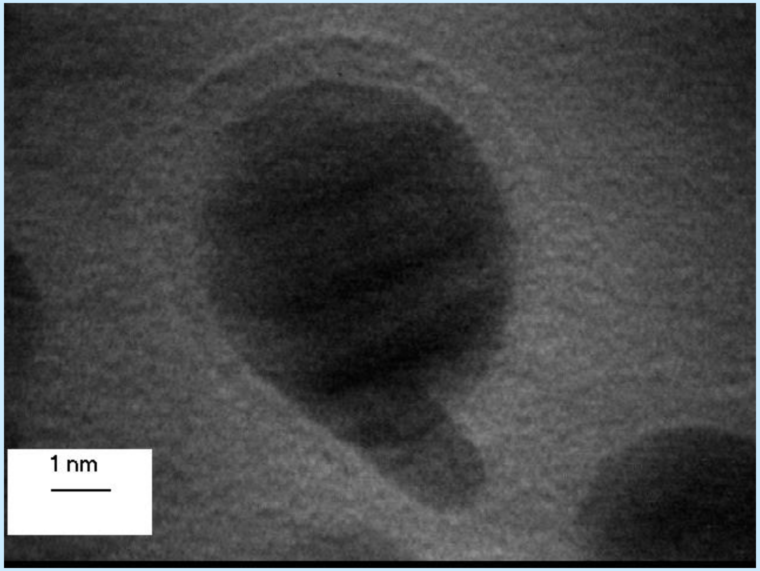
↓

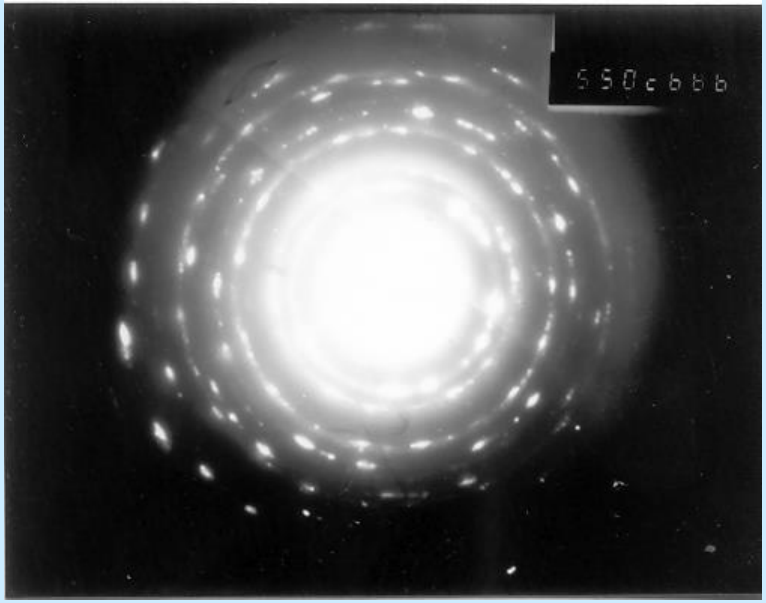
Sample ← **Hot Pressed**



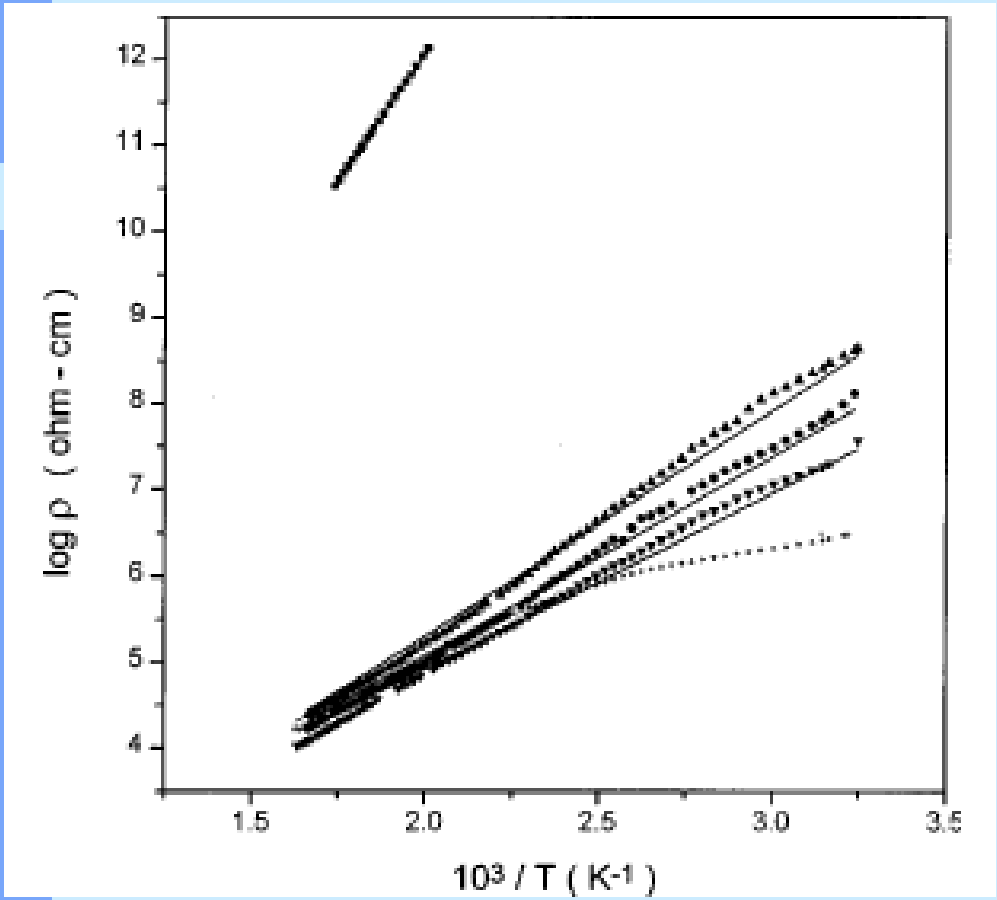
COPPER CORE COPPER OXIDE SHELL – INTERFACIAL AMORPHOUS PHASE

SPECIMEN REDUCED AT923K / 30MIN + OXIDIZED AT 823K / 30MIN





COPPER CORE COPPER OXIDE SHELL-INTERFACIAL AMORPHOUS PHASE



Variation of log resistivity as a function of inverse temperature for different samples.

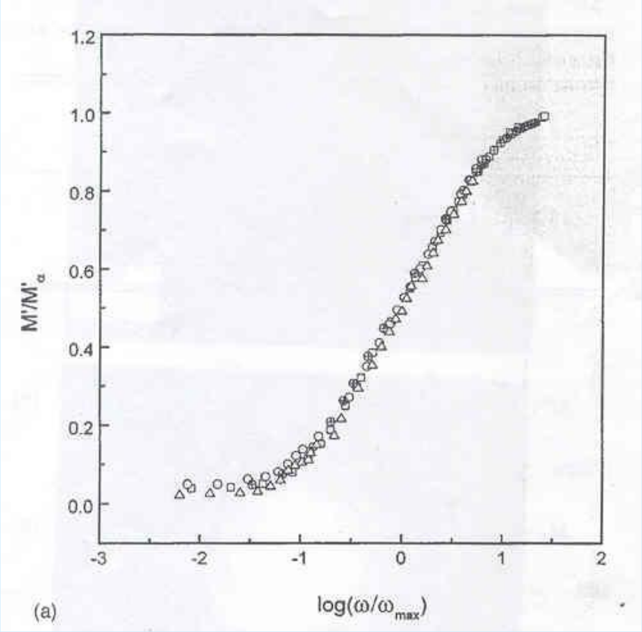
Das/Chakravorty Appl.Phys.Lett. <u>76</u> ,1273 (2000)

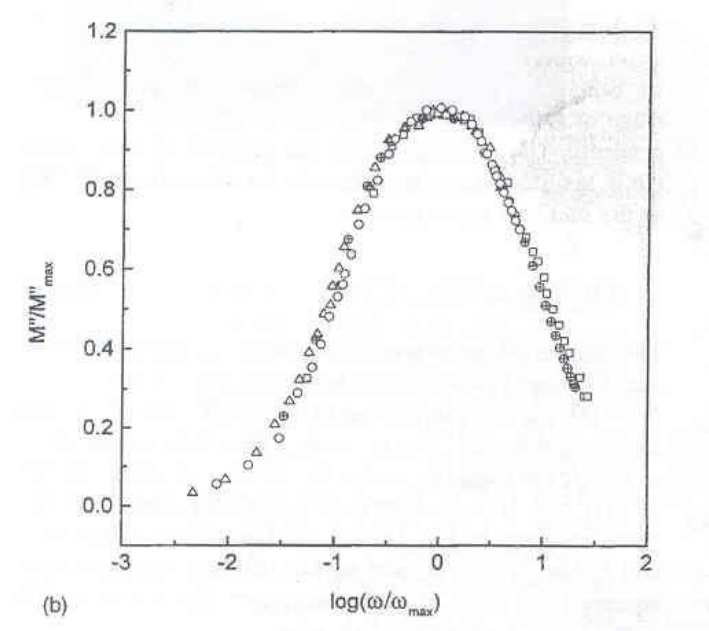
COPPER CORE COPPER OXIDE SHELL – INTERFACIAL AMORPHOUS PHASE

NORMALIZED PLOTS OF M\` AND M\`\`

SPECIMEN REDUCED AT 923K / 30 MIN + OXIDIZED AT 723K / 30 MIN

KWW FUNCTION : $F(t) = \exp[-(t/\tau_R)^{\beta}]$





COPPER CORE COPPER OXIDE SHELL – INTERFACIAL AMORPHOUS PHASE

Model	N/Wt	β_1	$10^{-5}\ \rho_0$	$10^6\ \tau_o$ (s)	$\varepsilon_{D\infty}$	$\varepsilon_{C1\infty}$	$10^5\ A_{SC}$	γ_{SC}	$100S_F$	−FQF
CK1	12/P	{0.191}	3.42	[0.013]	72.5	0.754	⋯	⋯	2.98	89
CK1	12/M	{0.190}	3.33	[0.009]	74.1	0.602	⋯	⋯	2.34	124
CK1	10/P	[0.450]	3.05	[17.3]	{56.8}	16.3	⋯	⋯	1.87	96
CK1	10/M	{0.371}	3.04	[5.50]	{64.7}	8.49	⋯	⋯	1.52	119
CK1	10/P	(2/3)	3.06	135	{11.4}	66.0	⋯	⋯	2.60	83
CK1	10/M	(2/3)	3.02	118	{19.7}	58.7	⋯	⋯	1.93	114
CK1S	10/M	(2/3)	2.49	[59.5]	56.0	35.9	{1.17}	0.66	0.84	141
CK1S	10/M	0.676	2.55	68.3#	51.3#	39.6	(1.81)	0.64	0.90	138
CK1	10/P	(1/3)	3.10	2.94	65.8	6.43	⋯	⋯	1.97	94
CK1	10/M	(1/3)	3.06	2.67	67.4	5.90	⋯	⋯	1.53	120
CK1S	10/M	(1/3)	2.58	{1.40}	82.0	3.96	{1.53}	0.65	0.90	137
CK1S	10/M	0.438	2.57	8.56	76.4	9.92	(1.53)	0.66	0.77	143
CK1S	12/P	0.333	2.82	2.14	73.9	5.14	[1.42]	0.70	2.03	106
CK1S	12/P/Y	{0.331}	2.97	[2.46]	{69.8}	5.90	[1.58]	{0.73}	2.03	106

Macdonald Basu Chakravorty , J.Chem. Phys. 122, 241703,(2005)

Fe - Fe_3O_4 - SiO_2 Gel Nanocomposites

Target Composition :55 Fe_2O_3. 45 SiO_2 (mol %)

Sol^n A :60 ml C_2H_5OH, 10ml H_2O, 23.17 gm $FeCl_3$

Sol^n B :90 ml C_2H_5OH, 15ml H_2O, 1 ml HCL
26.2 ml $Si(OC_2H_5)4$

Sol^n. A + Sol^n. B

↓

Ref. Sample ← (1123K / 2hr) 2 weeks for gelation

↓

Powder Hot Pressed (Metallic Conduction) ← Redcn in H_2 923 K / ½ hr

↓

Oxdn 573 K / ½ hr

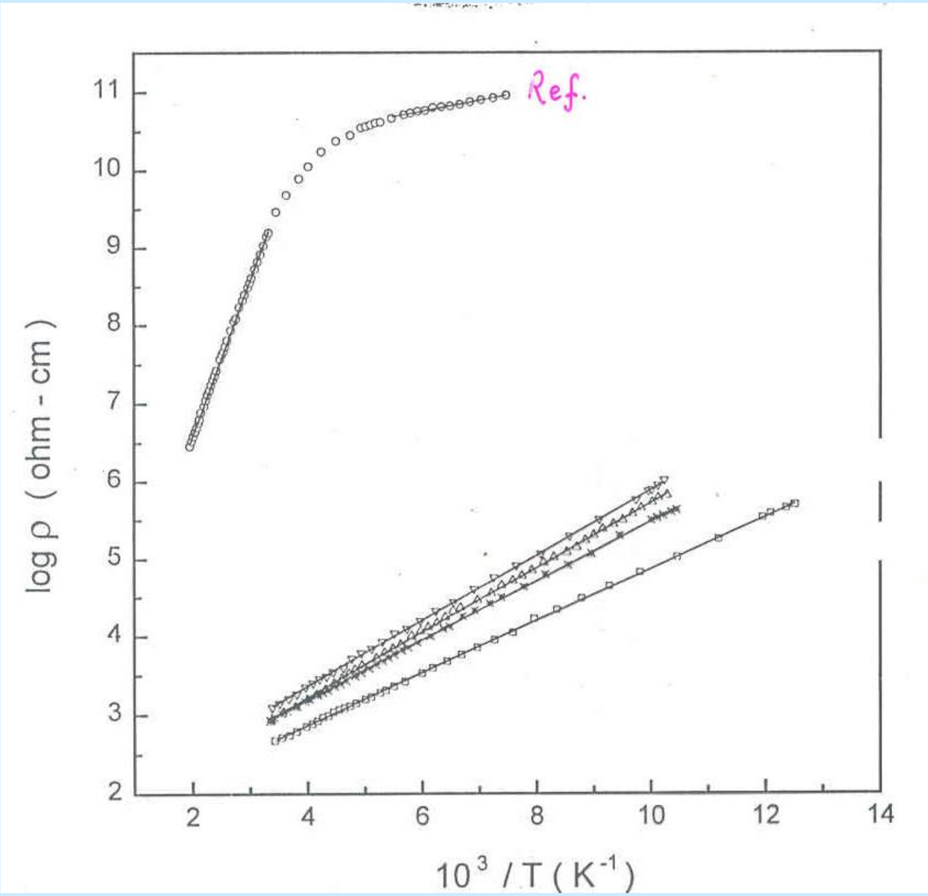
↓

Powder Hot Pressed
923K / 5 min

$Fe - Fe_3O_4 - SiO_2$ Gel Nanocomposites

Heat treatment Schedule for gel powder before hot pressing	Median Diameter X (nm)	Geometric Standerd Deviation σ
Reduced at 923 K / ½ hr	5.3	1.4
Reduced at 923 K / ½ hr Oxidized at 823 K / ½ hr X	4.9	1.4
Reduced at 923 K / ½ hr Oxidized at 1023 K / ½ hr	4.6	1.4
Reduced at 923 K / ½ hr Oxidized at 1123 K / ½ hr	4.4	1.4
Reduced at 923 K / ½ hr Oxidized at 1123 K / ½ hr	4.2	1.4
Reduced at 923 K / ½ hr Oxidized at 1123 K / ½ hr	4.1	1.4

$Fe\text{-}Fe_3O_4/SiO_2$ Nanocomposites



∇ 4.9 nm
Δ 4.6 nm
★ 4.4 nm
w/w 4.2 nm

Das et al J.Appl.Phys. 914573 (2002)

$Fe - Fe_3O_4 - SiO_2$ Gel Nanocomposites

speci men	W (cV)	α (A^{o-1})	R (A^o)	C	ν_o (s^{-1})	ε_ρ
Ref	0.39	0.95	4.7	0.99	$1.2x10^{13}$	4.9
2	0.08	0.89	4.7	0.99	$1.3x10^{13}$	23.8
3	0.08	0.86	4.8	0.99	$1.2x10^{13}$	23.3
4	0.07	0.87	4.9	0.99	$1.1x10^{13}$	26.1
5	0.06	0.86	4.8	0.99	$1.3x10^{13}$	31.1

Small polaron Hopping

$$\rho = \frac{kTR}{\upsilon_o c^2 c(1-c)} \exp(2\alpha R) \exp(W/kT)$$

$$W \approx e^2 / 4\varepsilon_p \gamma_p$$

$$\gamma_p = \frac{1}{2} (\frac{\Pi}{6})^{1/3} R$$

SILVER / SILICATE GLASS CERAMIC NANOCOMPOSITES

COMPOSITION :

10 Na_2O, 34 BaO, 34 TiO_2,17 B_2O_3, 5 SiO_2

⇩

Heat treatment at 843 K and 963 K

⇩

Powdered samples ION Exchanged at 583 K / 6 Hrs

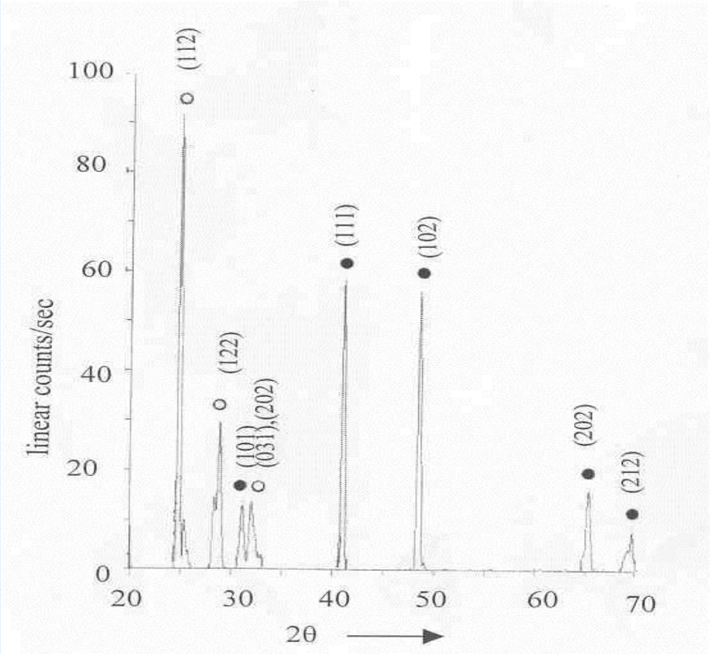
⇩

Reduction at 573 K / 5 Min.s

SILVER / SILICATE GLASS CERAMIC NANOCOMPOSITES

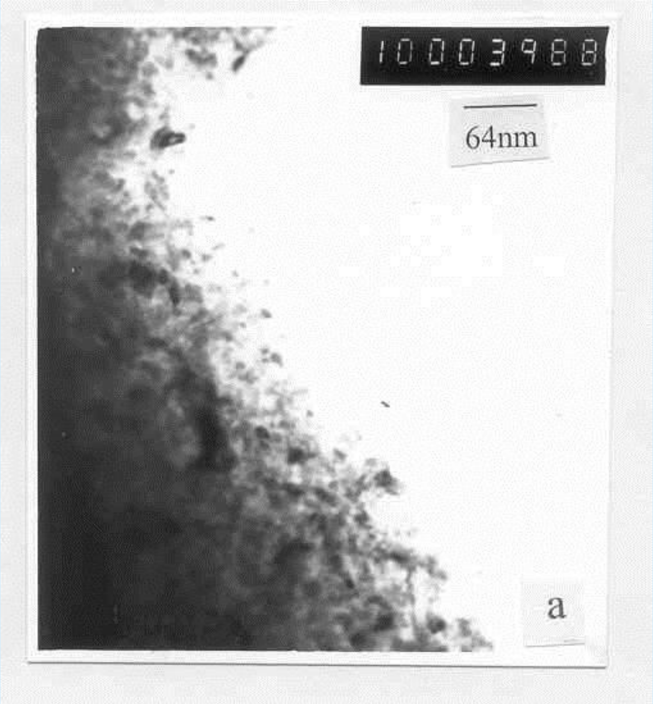
SEM Micrograph
of Glass Ceramic

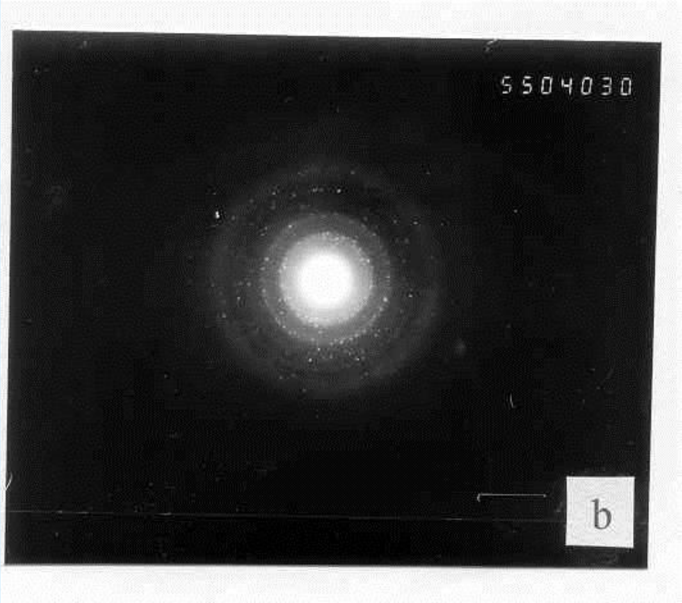
X Ray Diffractogram
of Glass Ceramic



Crystalline phases : $Na_2B_4O_7$; $BaTiO_3$

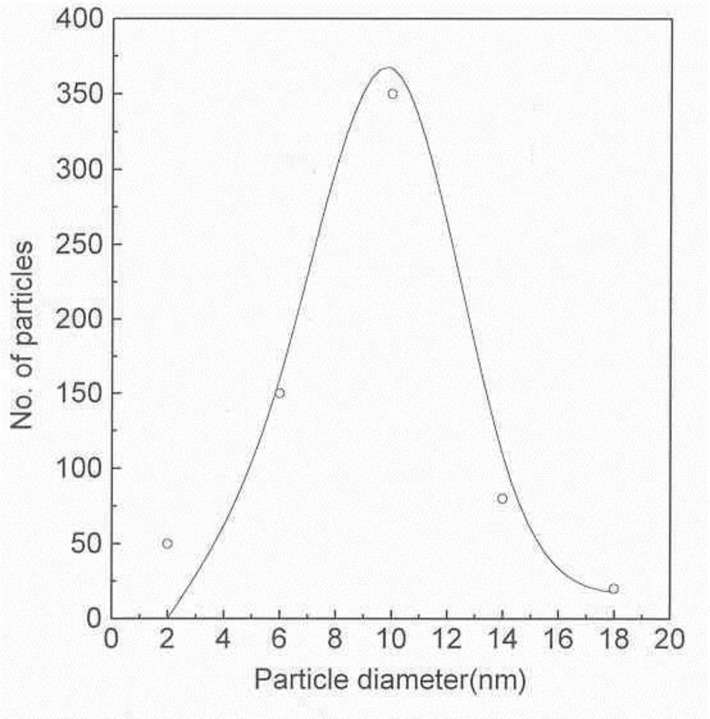
SILVER / SILICATE GLASS CERAMIC NANOCOMPOSITES





a) TEM of ION Exchanged and reduced Glass Ceramic
b) Electron Diffraction of (a)

SILVER / SILICATE GLASS CERAMIC NANOCOMPOSITES



Histogram of Silver Particle Size

SILVER / SILICATE GLASS CERAMIC NANOCOMPOSITES

Table II

Summary of heat treatment schedules for crystallization and median diameter $\bar{x}$ and geometric standard deviation σ obtained for different specimens after ion exchange/reduction treatment

Specimen No.	Heat Treatment Schedule	$\bar{x}$ (nm)	σ
1	843K for 2 hours + 963K for 10 min.	3.4	1.5
2	843K for 4 hours + 963K for 10 min.	4.6	1.3
3	843K for 6 hours + 963K for 15 min.	10.1	1.3
4	843K for 2 hours + 963K for 20 min.	13.2	1.4

Reduction in Hydrogen at 573 K / 5 Min.s

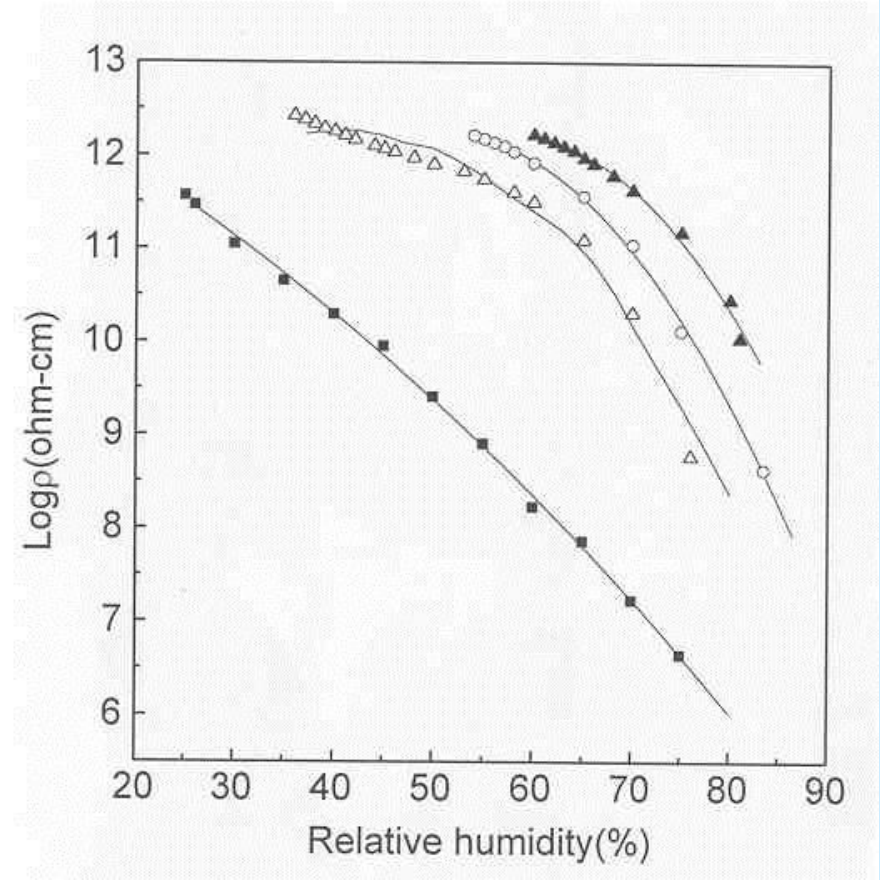
SILVER / SILICATE GLASS CERAMIC NANOCOMPOSITES

▲ 3.4 nm

○ 4.6 nm

■ 10.1 nm

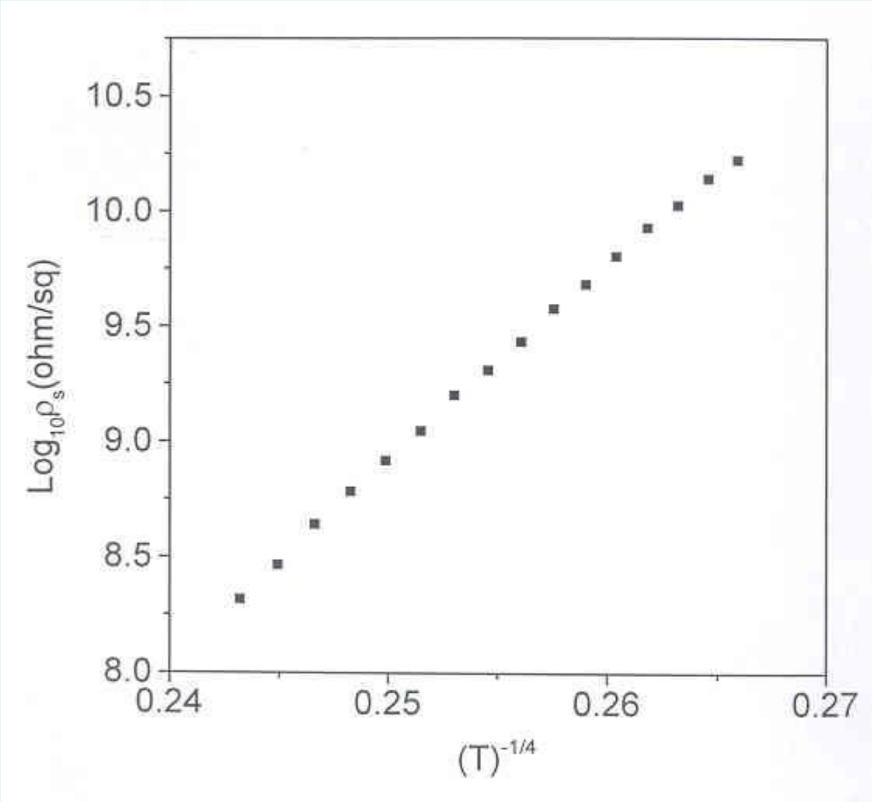
△ 13.2 nm



Resistivity vs. Relative Humidity

Pal et al J.Appl.Phys. 93, 4201 (2003)

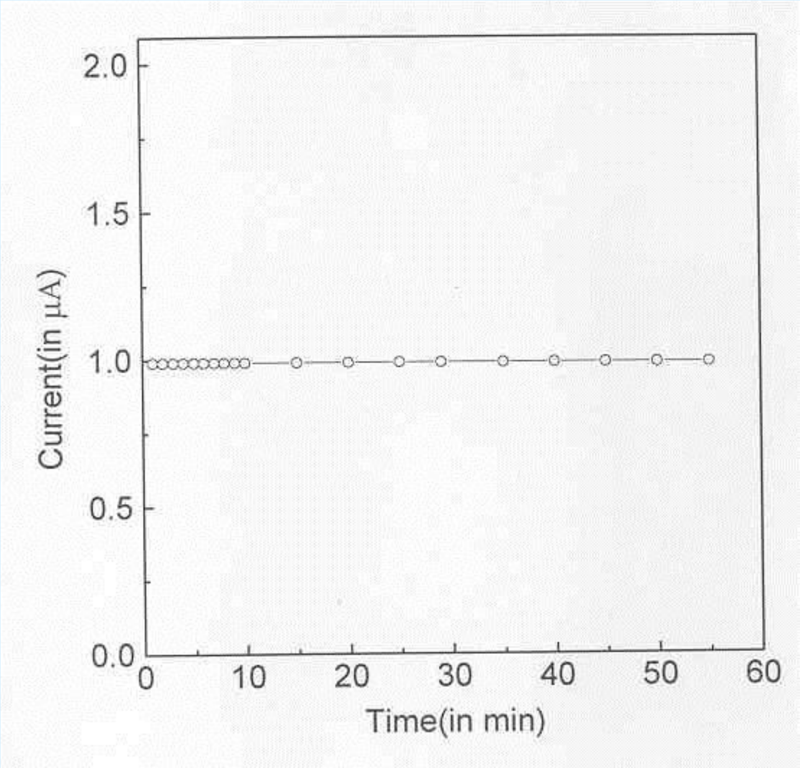
SILVER / SILICATE GLASS CERAMIC NANOCOMPOSITES



Surface Resistivity vs. $T^{-1/4}$

Particle Diameter 3.4 nm

SILVER / SILICATE GLASS CERAMIC NANOCOMPOSITES



Current vs. Time

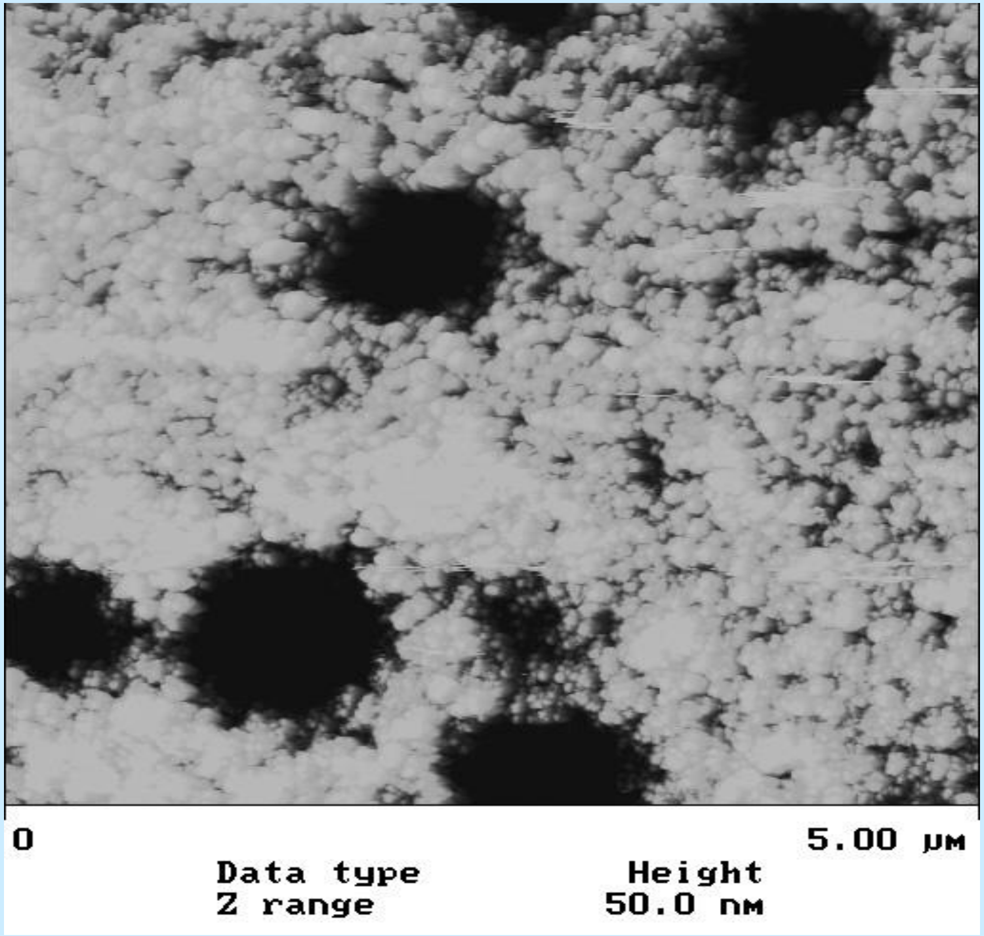
Silver Particle Diameter 10.1 nm

Relative Humidity 85 %

IRON-IRON OXIDE NANO CORE-SHELL STRUCTURE

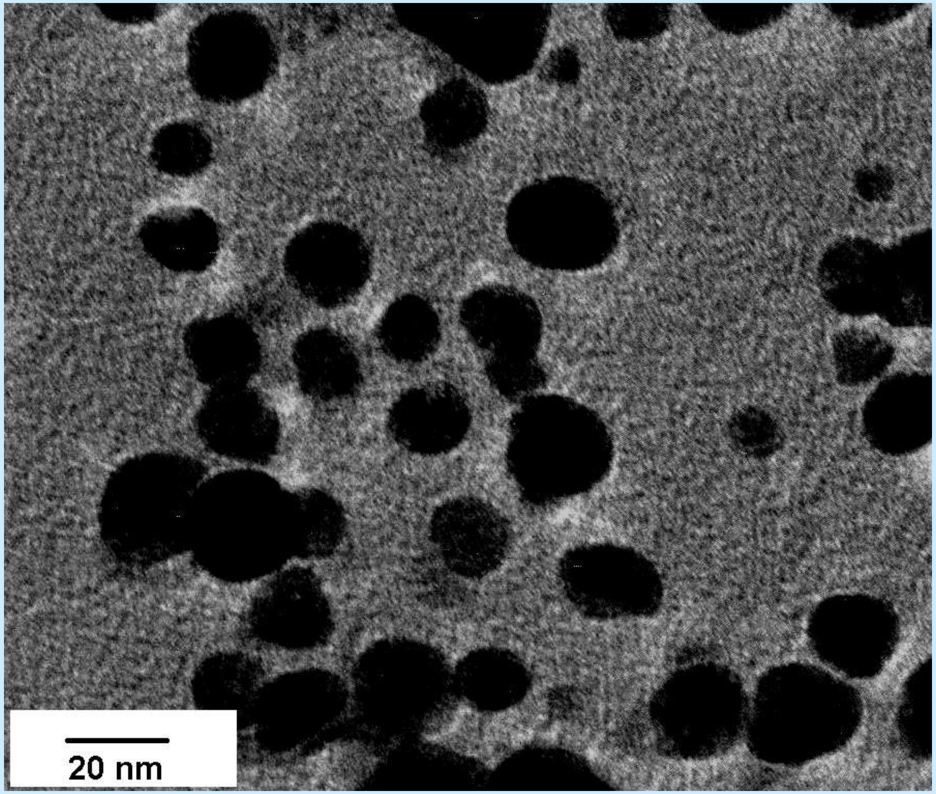
Optical micrograph of film with fractally grown Fe-Fe_3O_4 core shell structure

IRON-IRON OXIDE NANO CORE-SHELL STRUCTURE



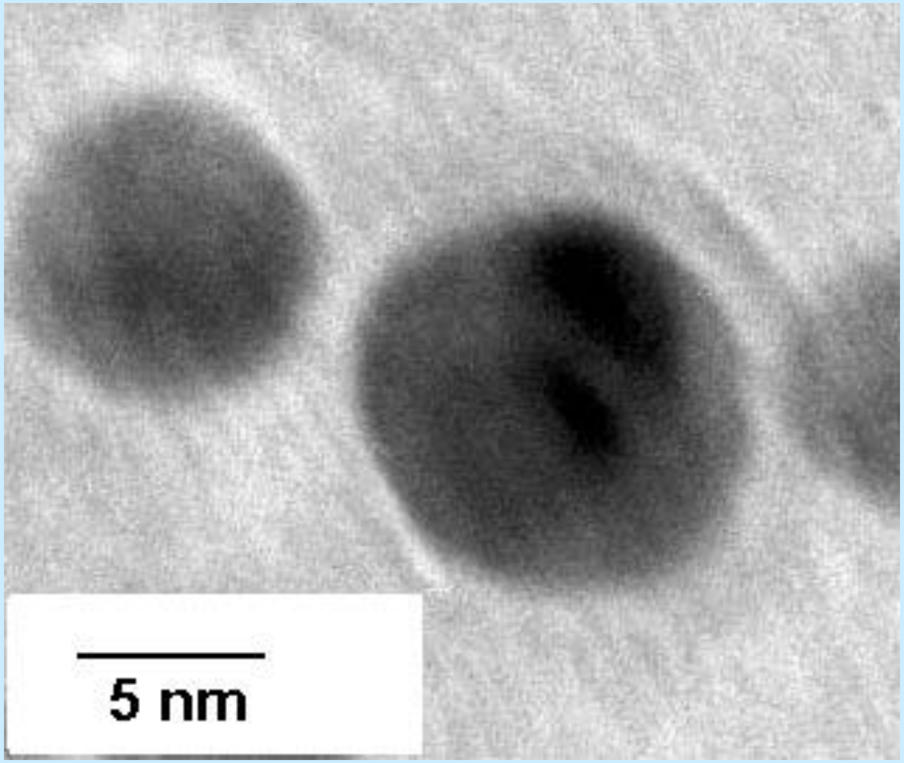
AFM micrograph

IRON-IRON OXIDE NANO CORE-SHELL STRUCTURE



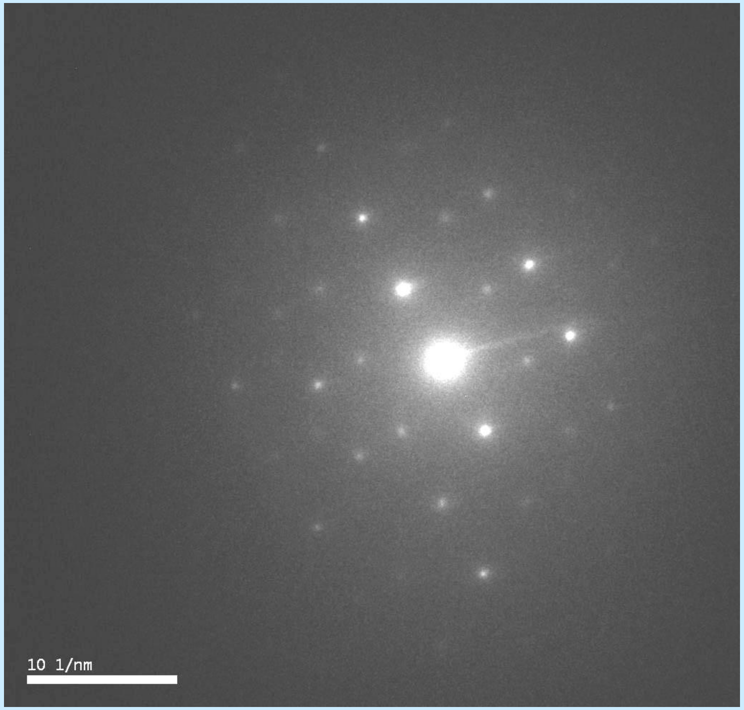
TEM of the specimen

IRON-IRON OXIDE NANO CORE-SHELL STRUCTURE



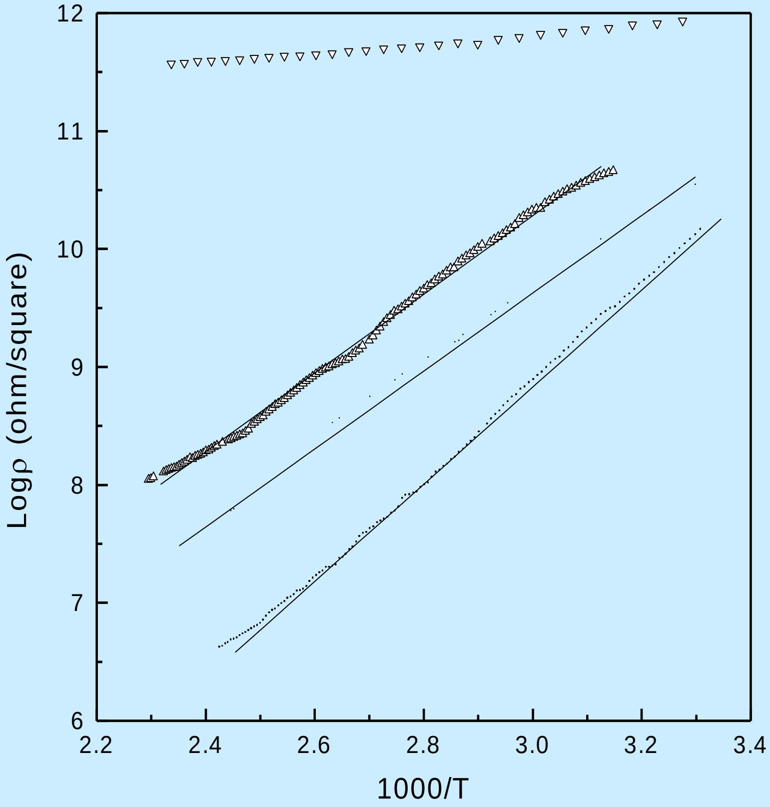
TEM of core shell structure

IRON-IRON OXIDE NANO CORE-SHELL STRUCTURE



Electron diffraction pattern IRON-IRON OXIDE NANO CORE-SHELL STRUCTURE

IRON-IRON OXIDE NANO CORE-SHELL STRUCTURE



Surface resistivity as a function of temperature

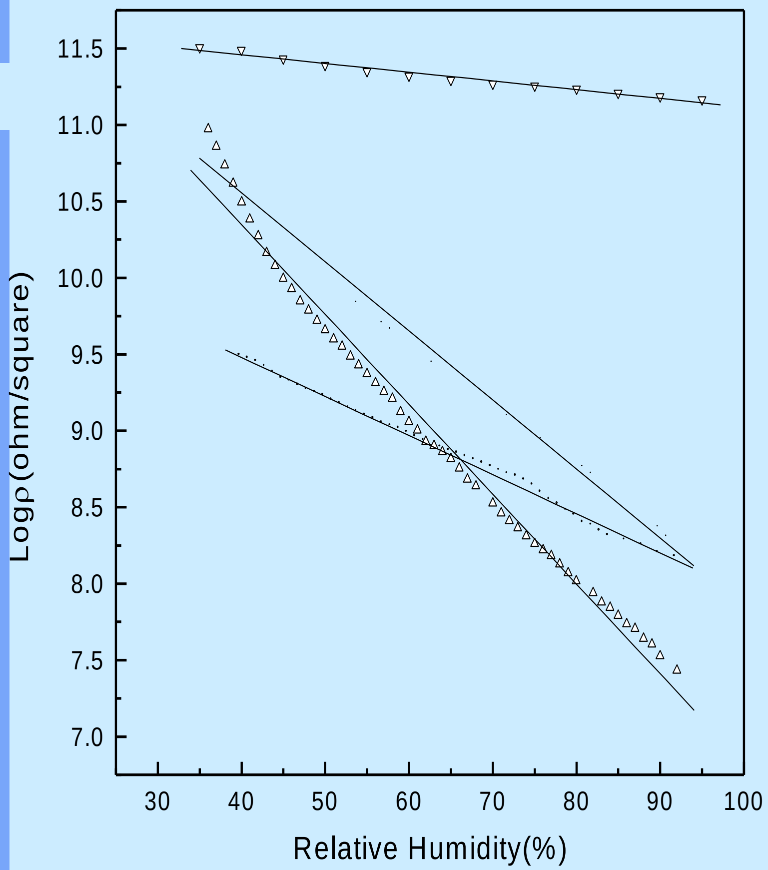
▽ Reference Specimen

O 1 hour oxidation

□ 2 hour oxidation

Δ 4 hour oxidation

IRON-IRON OXIDE NANO CORE-SHELL STRUCTURE



Surface resistivity vs. relative humidity

▽ Reference Specimen

O 1 hour oxidation

□ 2 hour oxidation

Δ 4 hour oxidation

Pal et.al. J.Appl.Phys.97,034311(2005)

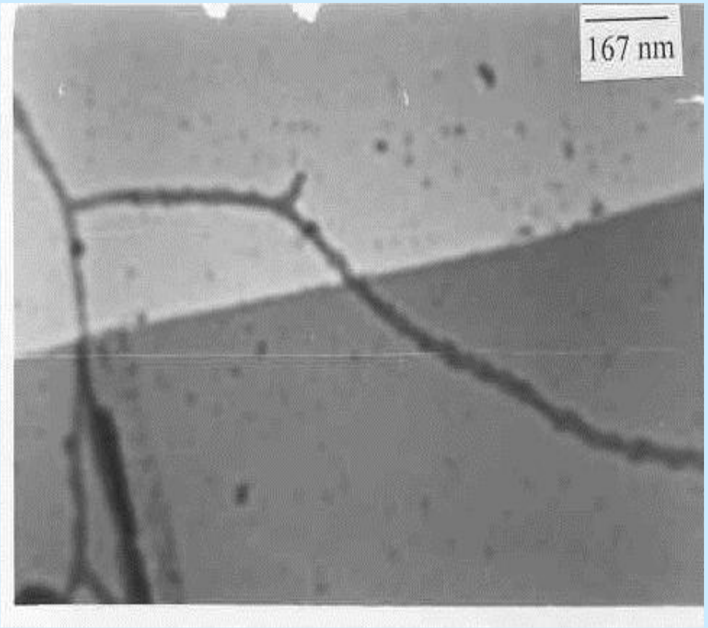
NANO INTERFACES IN GLASS METAL NANOCOMPOSITES

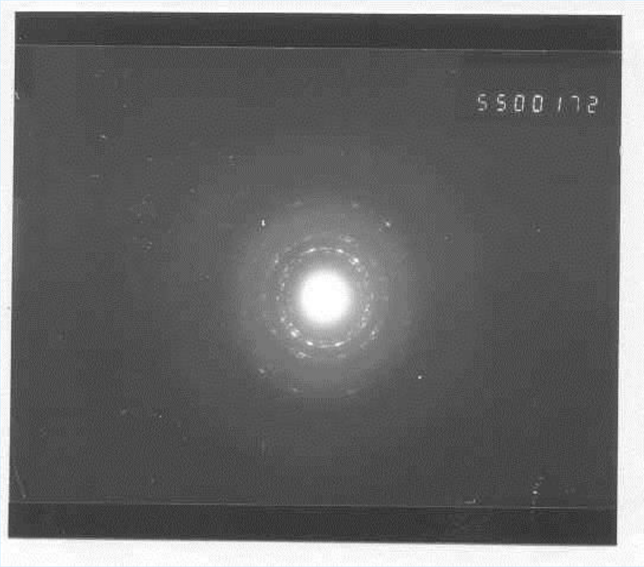
GLASS COMPOSITION : 30 Li_2O 12 CaO 3 Al_2O3 55 SiO_2

ION EXCHANGED IN $AgNO_3$ AT 573 K FOR 11 HRS

ELECTRODEPOSITION AT 600 K, 5 and 10 VOLTS FOR 10 HRS

NANO INTERFACES IN GLASS METAL NANOCOMPOSITES

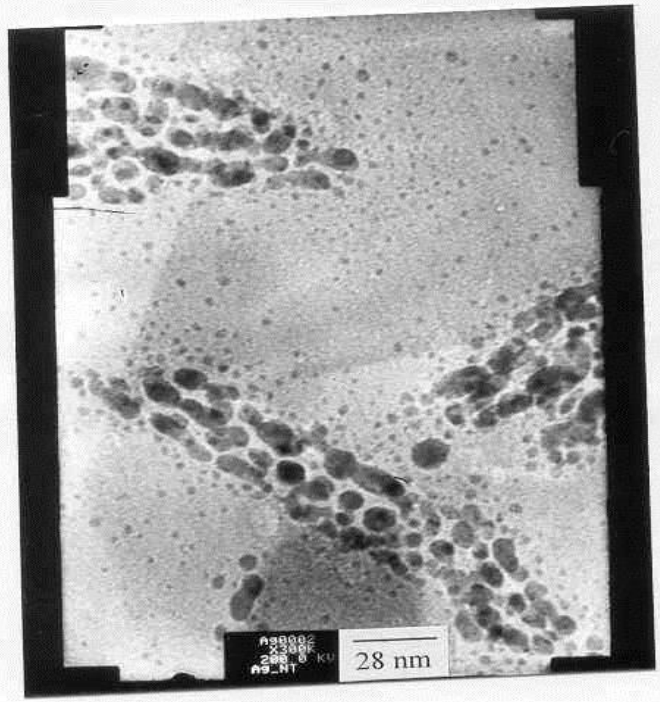




TEM

OF SILVER NANO ARRAYS

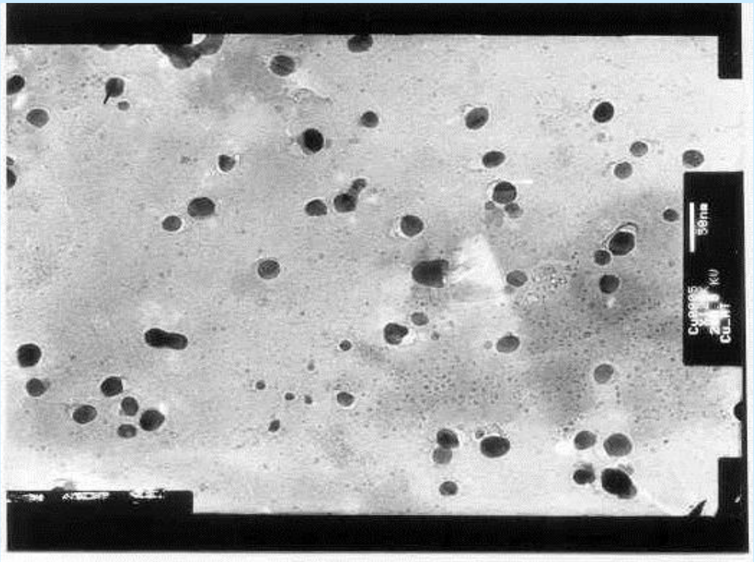
NANO INTERFACES IN GLASS METAL NANOCOMPOSITES

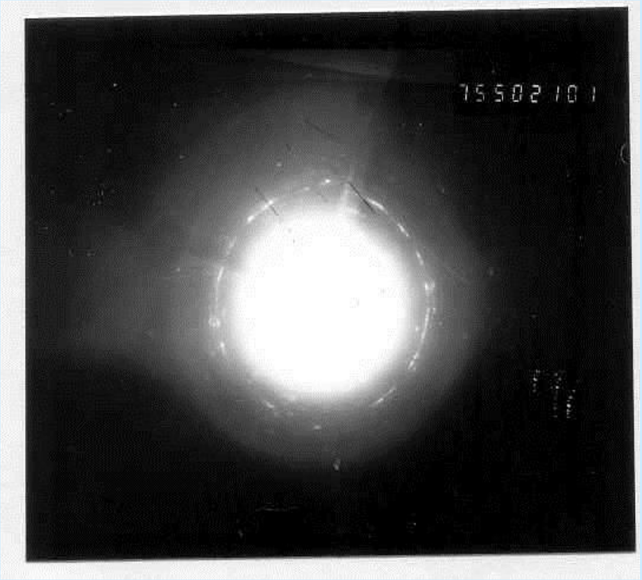


TEM OF NANO ARRAYS OF SILVER IN SILICATE GLASS

NANO INTERFACES IN GLASS METAL NANOCOMPOSITES

TEM OF SILICA GEL GLASS WITH COPPER NANO ARRAYS

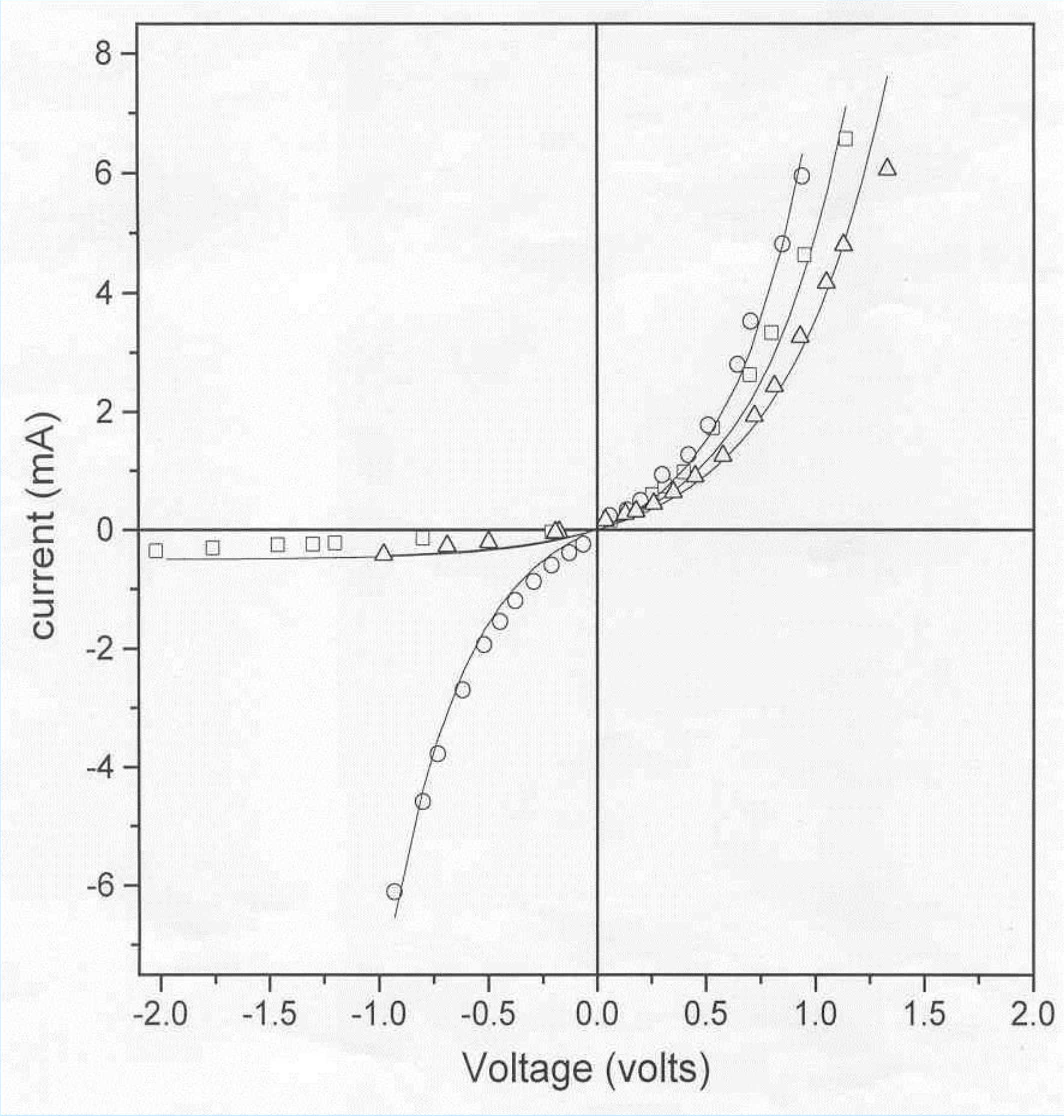


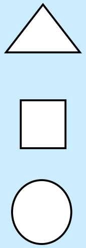


COMPOSITION : **$30Cu(NO_3)_2$ $70SiO_2$**

ELETRODEPOSITION VOLTAGE : 5 VOLTS

NANO INTERFACES IN GLASS METAL NANOCOMPOSITES





191 K

161 K

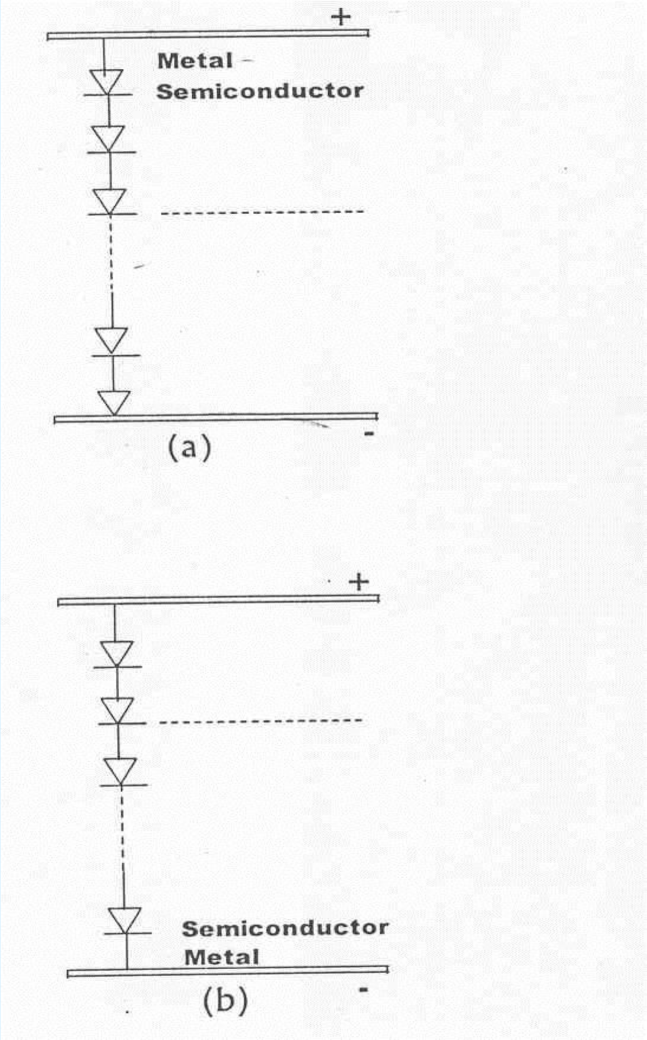
138 K

GLASS COMPOSITION

$30Li_2O$ $12CaO$ $3Al_2O_3$ $55SiO_2$

ELECTRO DEPOSITION
VOLTAGE : 5 VOLTS

NANO INTERFACES IN GLASS METAL NANOCOMPOSITES

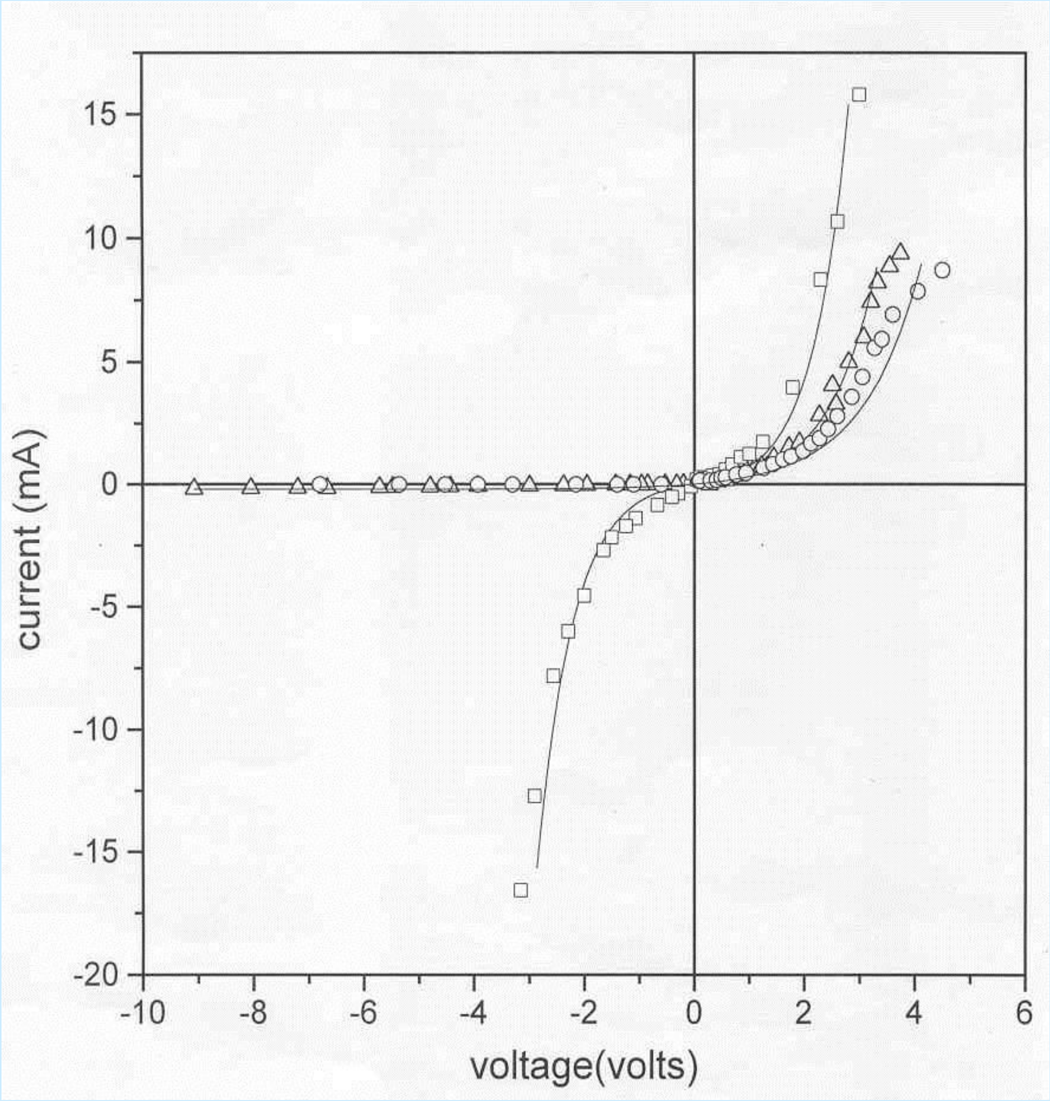


DIODE LIKE BEHAVIOUR

SCHEMATIC REPRESENTATION OF
METAL SEMICONDUCTOR
NANO JUNCTION ARRAYS

SYMMETRICAL NON LINEAR V - I

NANO INTERFACES IN GLASS METAL NANOCOMPOSITES



△ 208 K

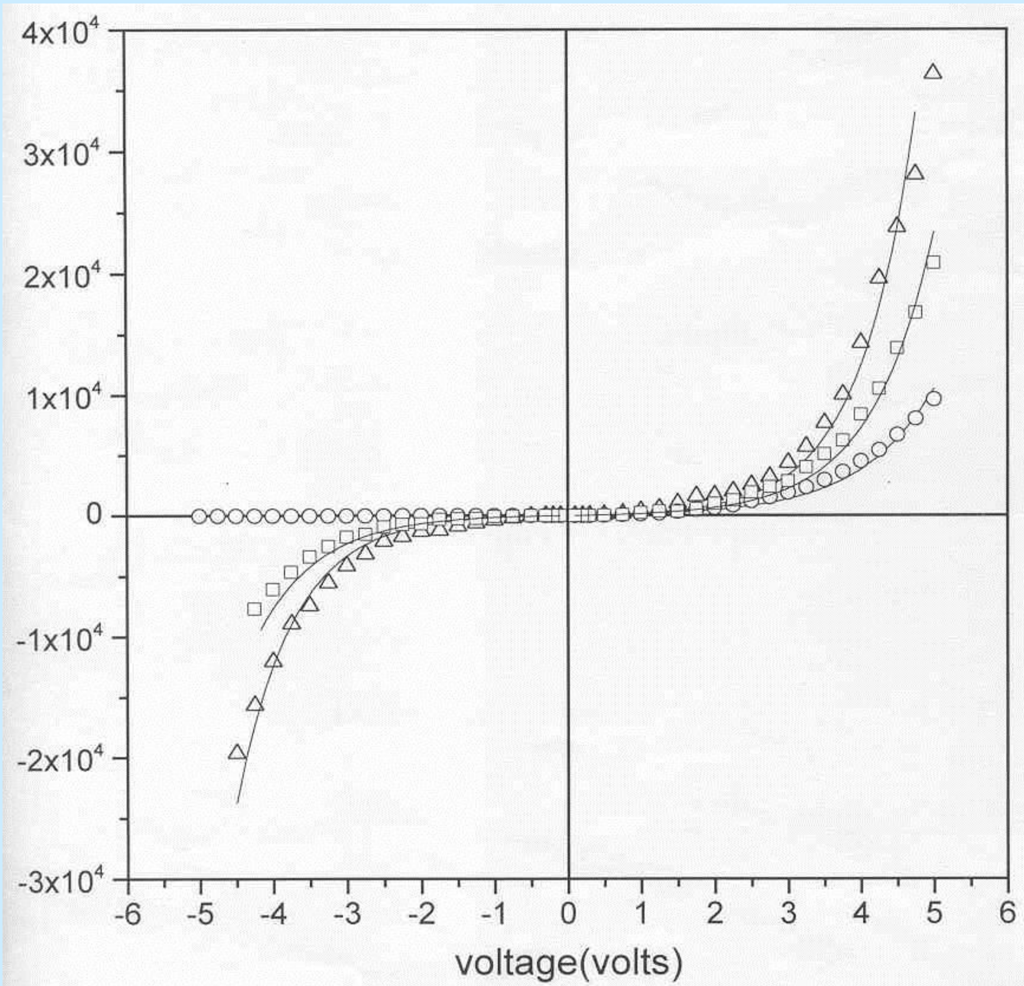
○ 167 K

□ 125 K

30 LI_2O 12CaO $3Al_2O_3$ $55SiO_2$

ELECTRODEPOSITION
AT 10 VOLTS

NANO INTERFACES IN GLASS METAL NANOCOMPOSITES



○ 275 K

□ 238 K

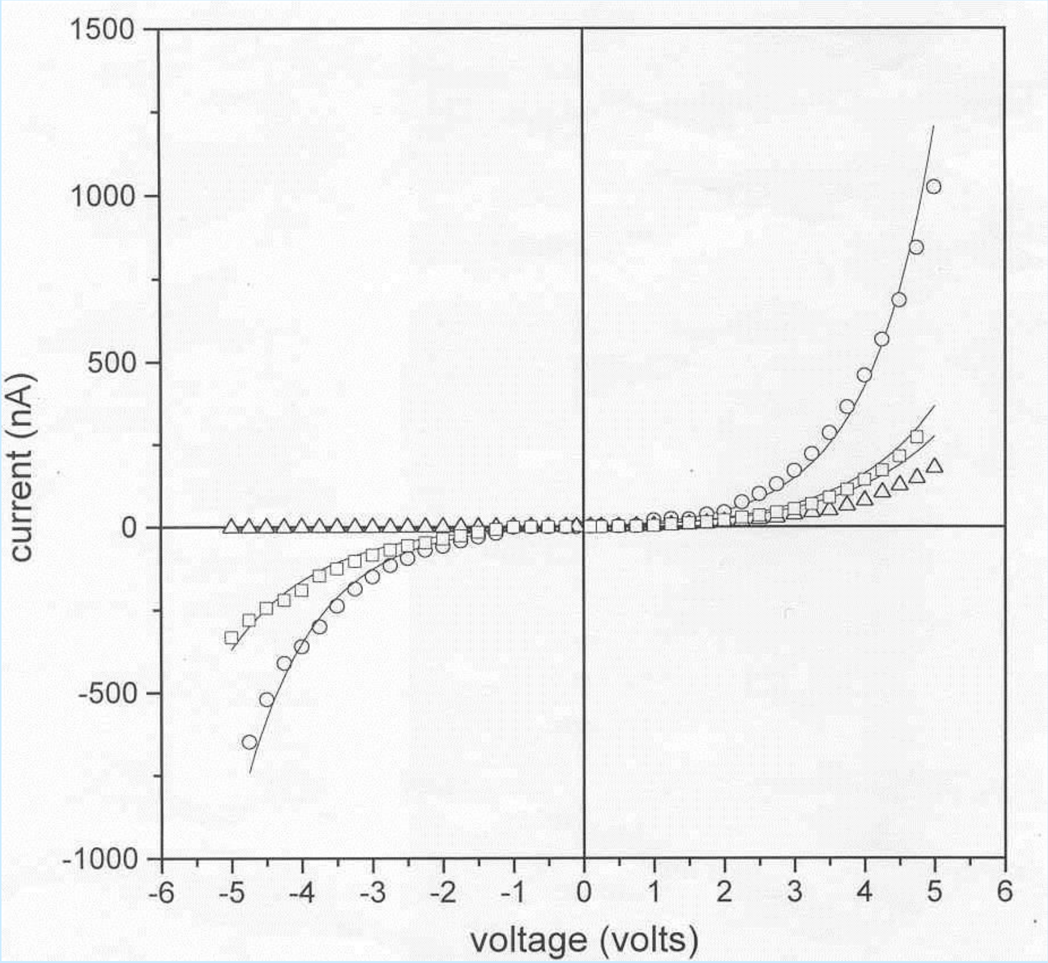
△ 213 K

$30Cu(NO_3)_2 . 70SiO_2$ GEL

ELETRODEPOSITION
AT 5 VOLTS

Dan et al J.Appl.Phys. 93,4794 (2003)

NANO INTERFACES IN GLASS METAL NANOCOMPOSITES



285 K

265 K

208 K

$30Cu(NO_3)_2 \,.\, 70SiO_2$ GEL

ELETRODEPOSITION
AT 10 VOLTS

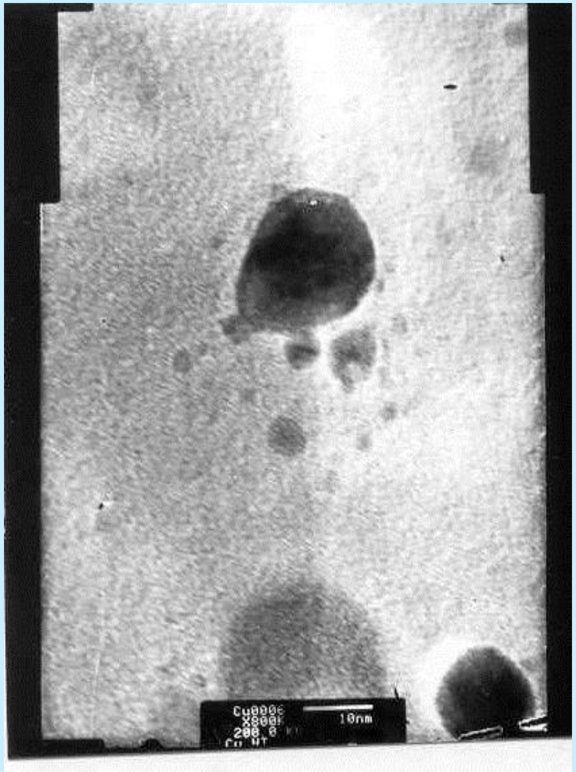
NANO INTERFACES IN GLASS METAL NANOCOMPOSITES

DATA FITTED TO

$$I = I_0\left[\exp\left(\frac{eV}{nkT}\right) - 1\right]$$

COMPOSITION	ELECTRO DEPOSITION VOLTAGE	I_0 (Amp)	n
1	5	0.5×10^{-3}	30
1	10	0.2×10^{-3}	60
2	5	0.7×10^{-7}	42
2	10	0.07×10^{-7}	55

NANO INTERFACES IN GLASS METAL NANOCOMPOSITES



ELECTRODEPOSITION
VOLTAGE 5 VOLTS

TEM OF A NANO INTERFACE

BETWEEN TWO COPPER PARTICLES

CONCLUSIONS

- Silicate glasses can be used as effective templates for nanostructure growth
- Glass nanocomposites show novel properties
- New functionalities can be generated by using a nanocomposite approach in glasses

THANK YOU