SYNTHESIS AND CHARACTERIZATION OF NANOTUBES AND NANOPARTICLES OF ALUMINIUM NITRIDE

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Electron Temperature Calculation

Electron temperature calculation for arc (collision dominated) plasma was done by the following method. It was seen that the average electron temperature varied between 7,000 K to 12,000K depending on the arc current.

Formula Used :

$$\frac{I_1}{I_2} = \frac{g_1 A_1 \lambda_1}{g_2 A_2 \lambda_2} \exp\left[-\frac{E_1 - E_2}{kT}\right]$$

Where :

I_1 and I_2 are the intensities of the lines 1 & 2

g_1 and g_2 are the degeneracy of lines 1 & 2

A_1 and A_2 are the transition probability of levels 1 & 2

E_1 and E_2 are the excitation energy of levels 1 & 2

I_1 = 82 I_2 = 36 λ_1 = 327 nm

g_1 = 3 g_2 = 5 λ_2 = 325.9 nm

E_1 = 13.2213 E_2 = 13.9287

$A_1 = 0.21 \times 10^8$/s $A_2 = 0.38 \times 10^8$/s

$$\frac{82}{36} = \frac{3 \times 0.21 \times 10^8 \times 325.9}{5 \times 0.38 \times 10^8 \times 327.0} \exp\left[-\frac{13.22 - 13.92}{kT}\right]$$

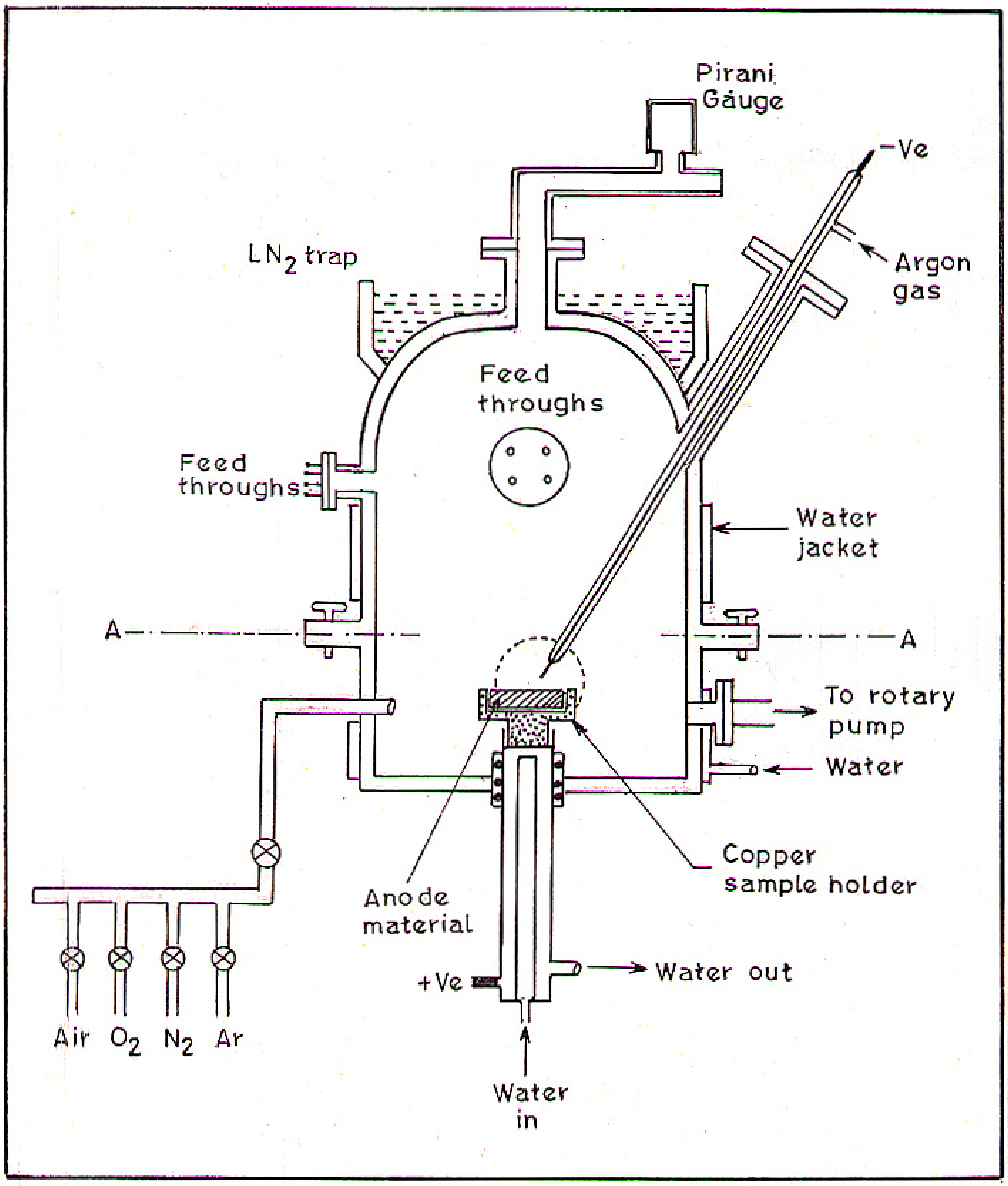
$$kT = \frac{0.7}{0.978} = 0.716 eV; \qquad T_e = 8294 K$$

ADVANTAGES OF PLASMA SYNTHESIS

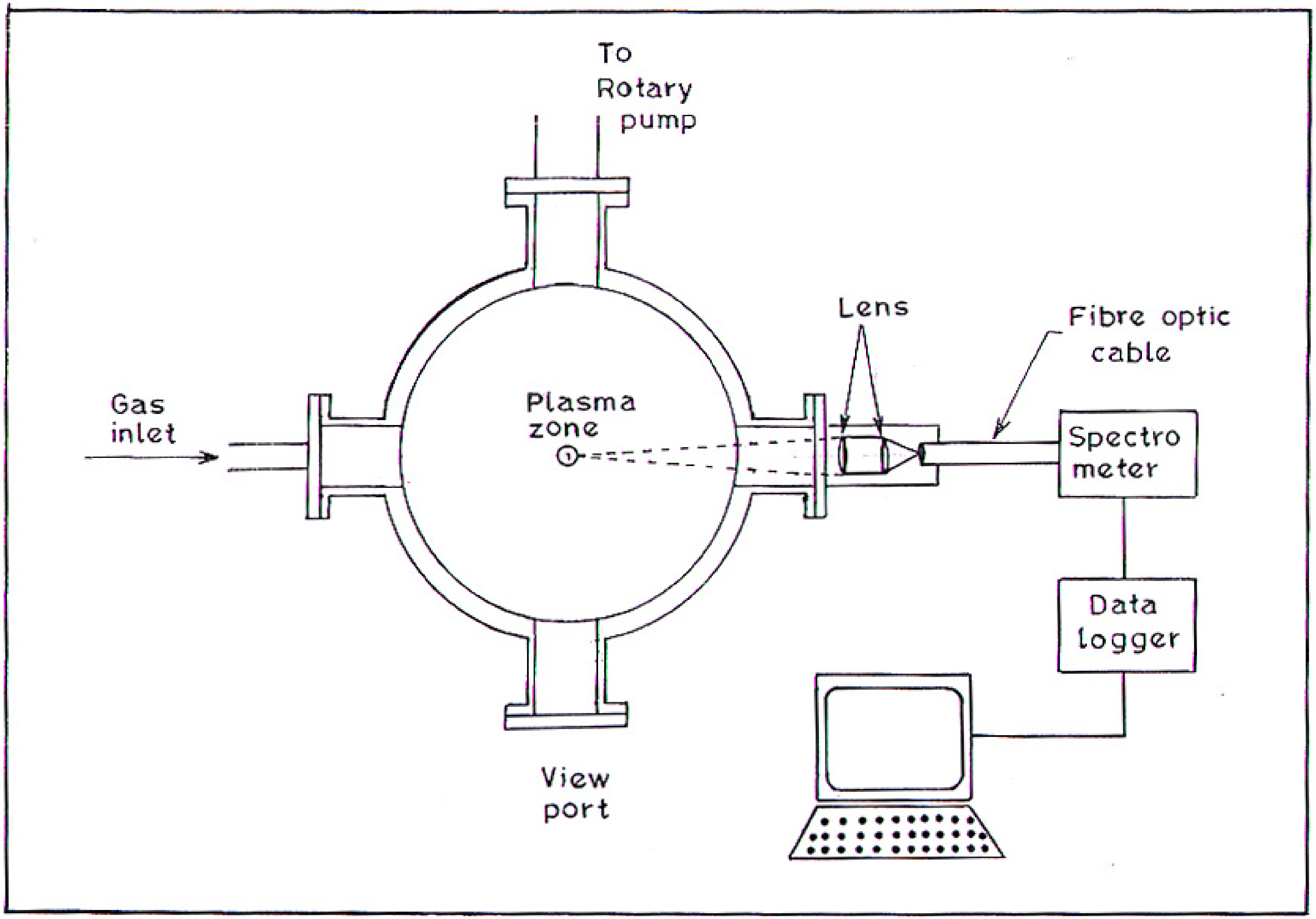
- High temperature reaction – Ceramics can also be synthesized
- This method also helps in the spectroscopic study of the reaction mechanism
- Wide range of materials can be synthesized without change in experiemental set up.
- Crystalline phases are obtained
- High purity
- Simple to Use
- High vacuum not necessary

SYNTHESIS PARAMETERS

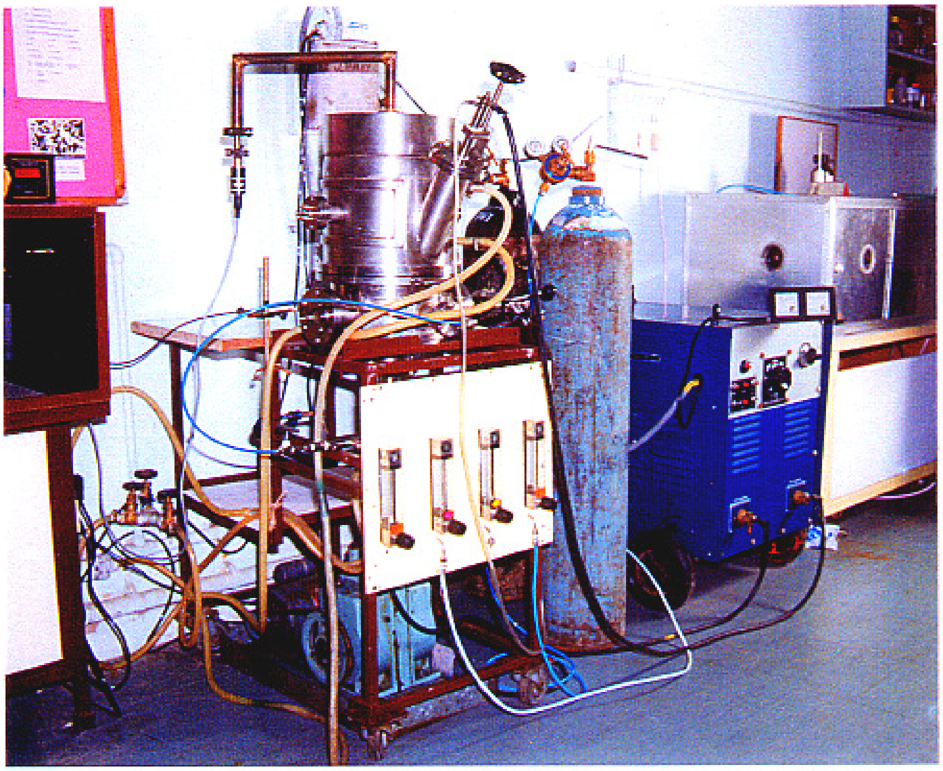
Type of plasma	:	DC Transferred Arc Plasma
Anode	:	Aluminium
Cathode	:	Tungsten (2 mm dia)
Arc Voltage	:	12 – 20 V (OCV – 70 V)
Arc Current	:	50A, 100 A, 150 A
Base Pressure	:	10^{-3} Torr
Operating Pressure	:	500 – 600 Torr
Chamber Volume	:	0.02 m^3
Reacting Gas	:	N_2 (Flow rate – 1.5 lit/min)
Plasma Gas	:	Argon (0.5 lit/min)

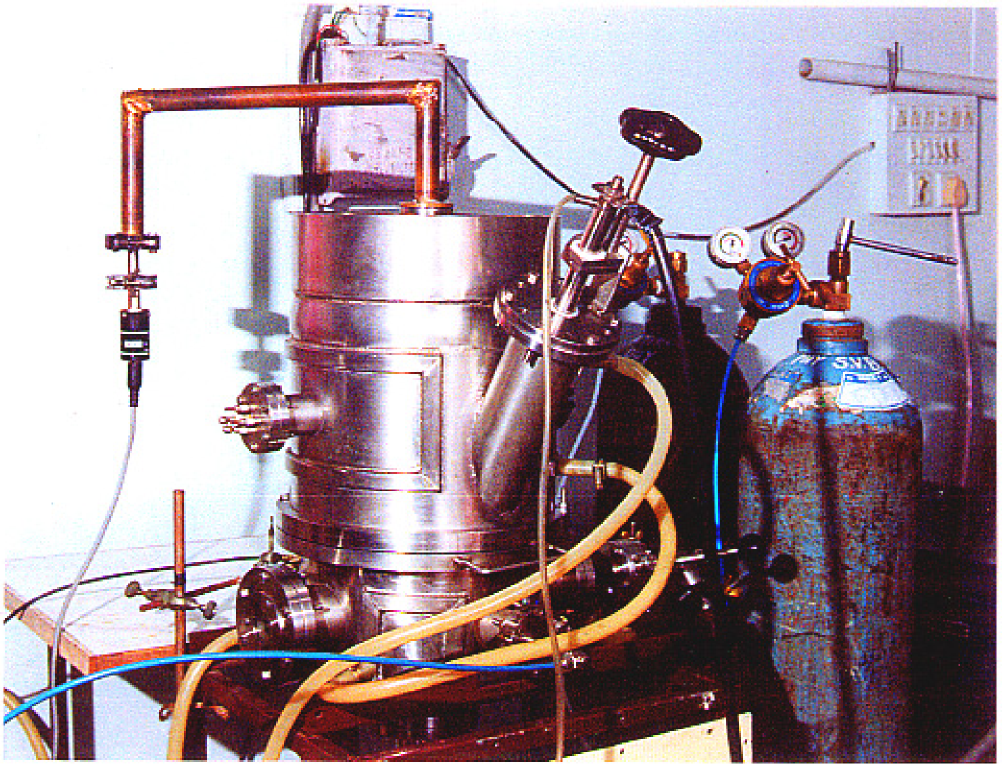


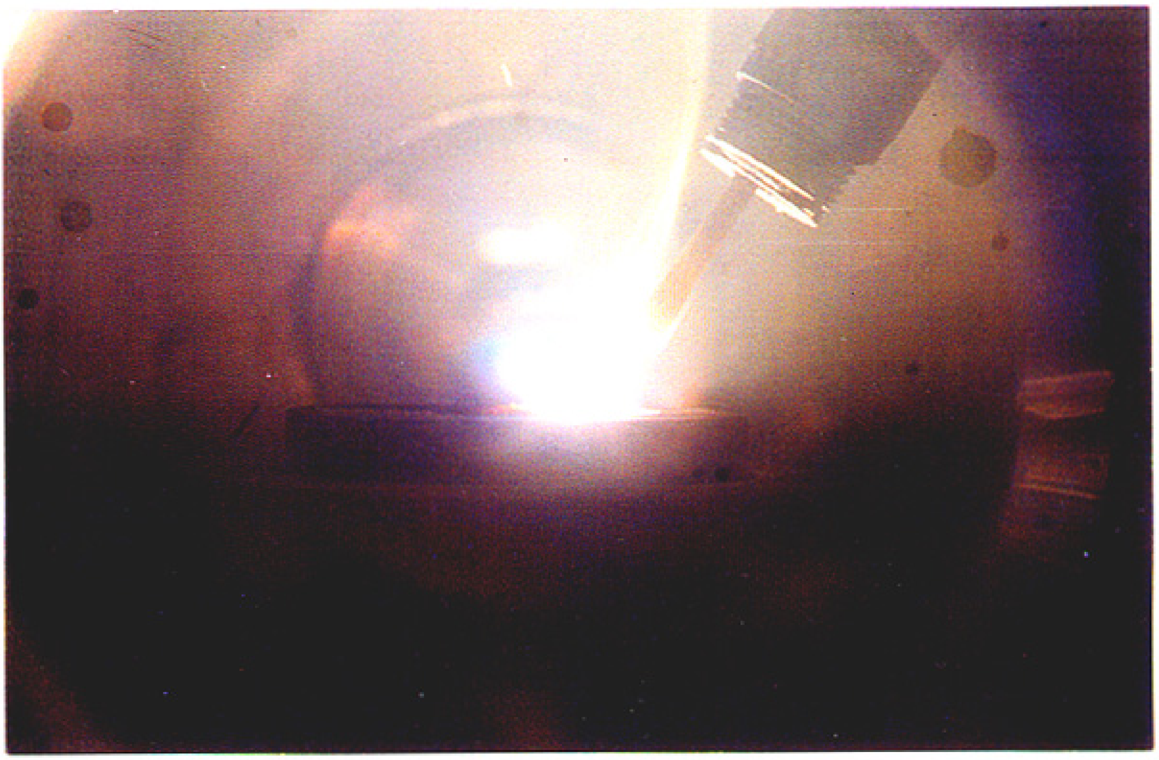
Pirani Gauge
-Ve
Argon gas
LN_2 trap
Feed throughs
Feed throughs
Water jacket
A
A
To rotary pump
Water
Copper sample holder
Anode material
Water out
+Ve
Water in
Air
O_2
N_2
Ar



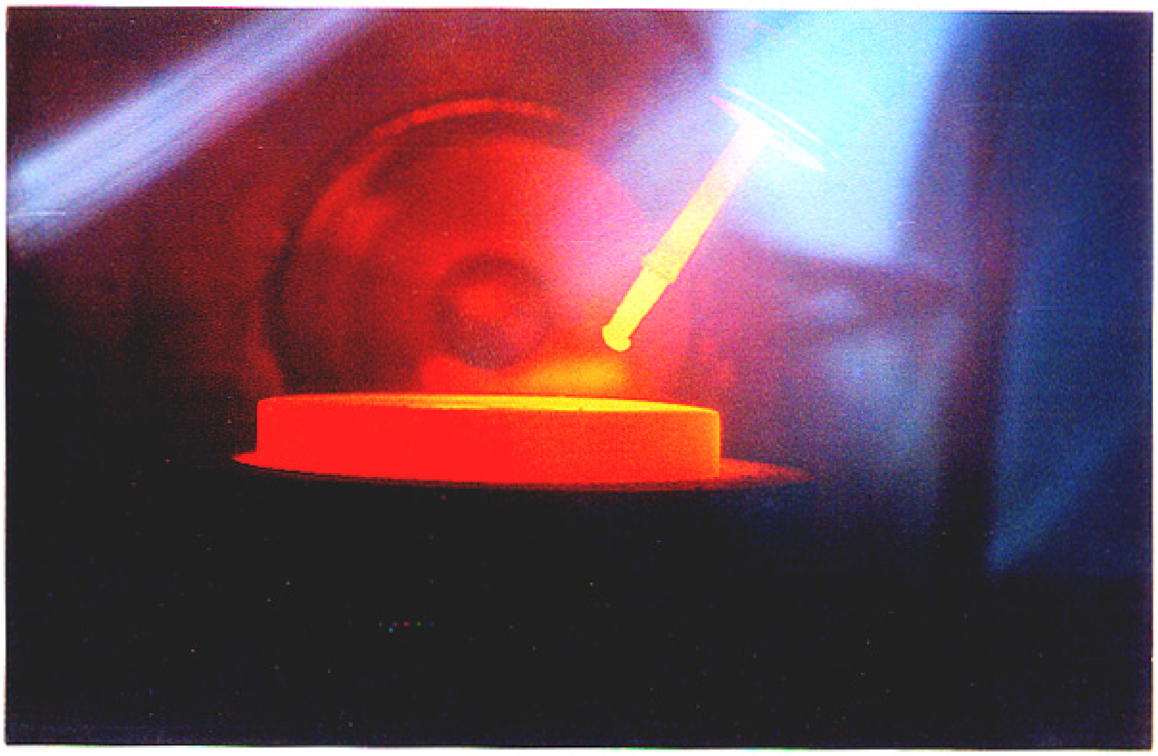
To
Rotary
pump
Lens
Fibre optic
cable
Gas
inlet
Plasma
zone
1
Spectro
meter
Data
logger
View
port





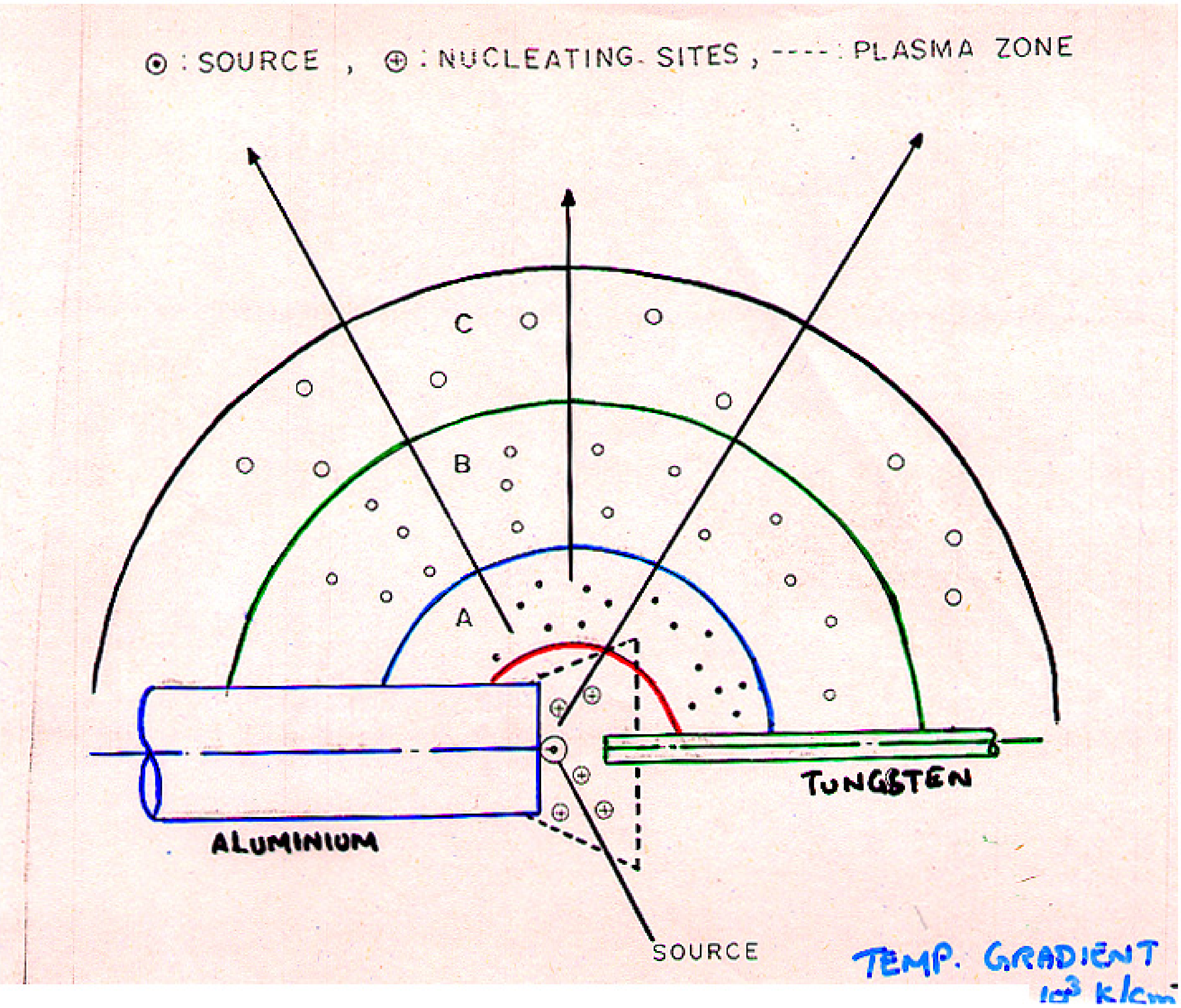


(a)



(b)

Fig. 5: Photograph showing the tungsten rod cathode and the graphite block anode (a) during arcing and (b) immediately after the arc is extinguished


⊙ : SOURCE , ⊕ : NUCLEATING SITES , ---- : PLASMA ZONE
C
B
A
ALUMINIUM
TUNGSTEN
SOURCE
TEMP. GRADIENT
10³ K/cm

NUCLEATION

- METAL ATOMS FROM THE SOURCE WILL RAPIDLY LOSE THEIR ENERGY
- METAL VAPOUR IS COOLED IN THE GAS
- COLLISSION FREE PATH IS VERY SHORT

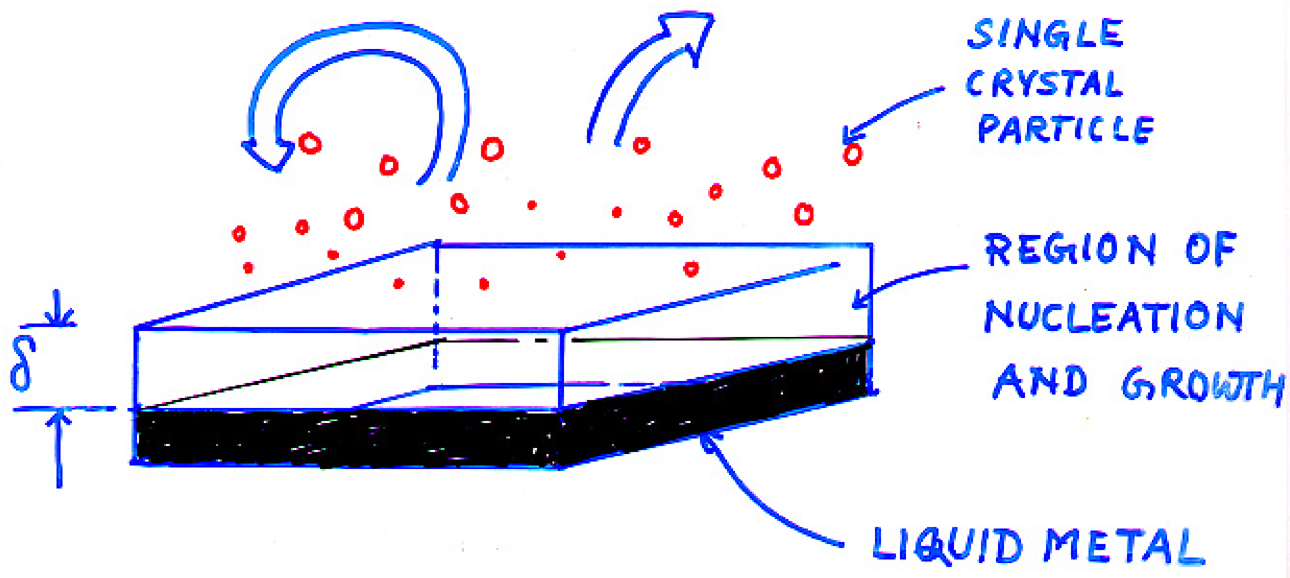
CRITICAL DIAMETER FOR EMBROY

$$x_{crit} = 4\,[\rho R T \ln (p_v / p_o)]^{-1}$$

ρ = density R = gas constant

p_v/p_o = Supersaturation ratio.

- HOMOGENEOUS NUCLEATION



GAS PHASE SYNTHESIS

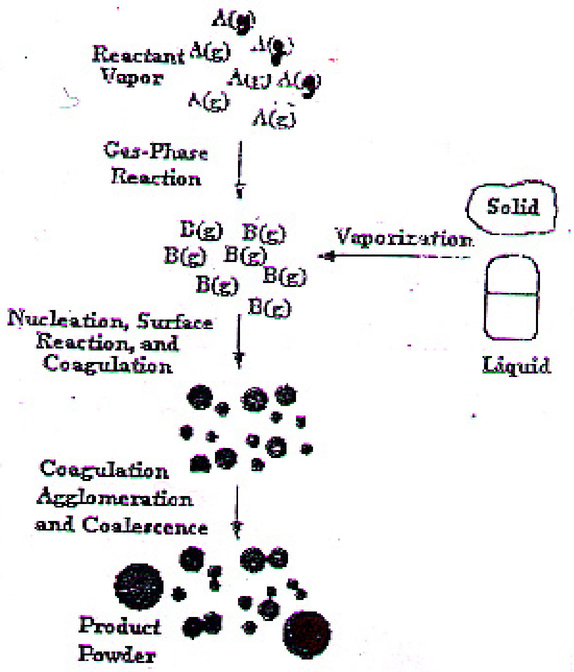


Fig. 2. Gas-to-particle conversion process.

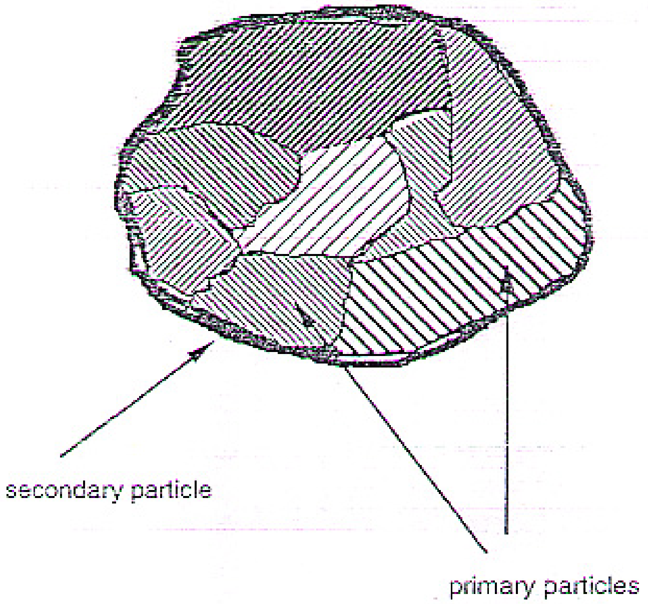


Figure 3.1. A schematic diagram showing the primary and secondary particles.

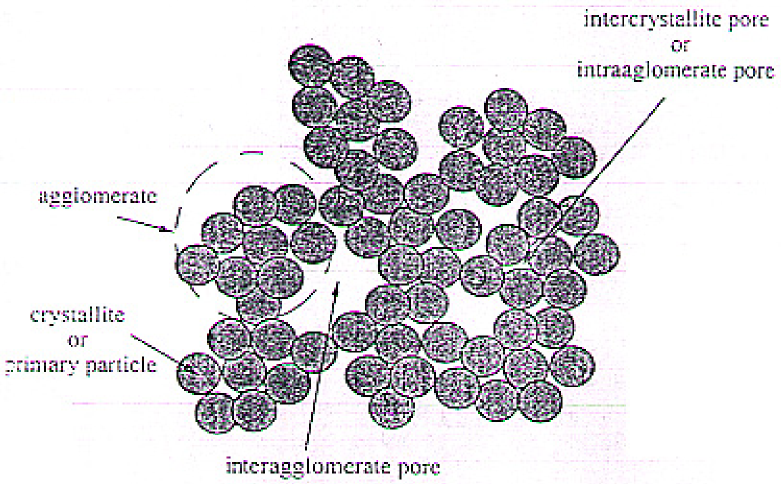


Figure 8.2. Schematic diagram of an agglomerated powder.

PROPERTIES OF AlN

* LARGE BANDGAP (~ 6.2 eV - BULK) SEMICONDUCTOR

* HIGH THERMAL CONDUCTIVITY. COEFFICIENT OF THERMAL EXPANSION (LOW) MATCHES WITH THAT OF SILICON

* POTENTIAL CANDIDATE FOR OPTO ELECTRONIC AND ELECTRO ACCOUSTIC DEVICES

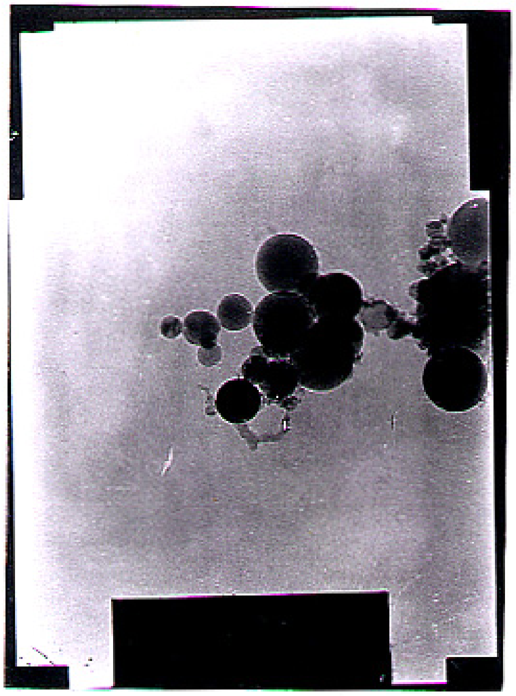
* PIEZOELECTRIC PROPERTY

* CHEMICALLY STABLE

* HEXAGONAL (STABLE) & CUBIC (METASTABLE) PHASES

I = 50A

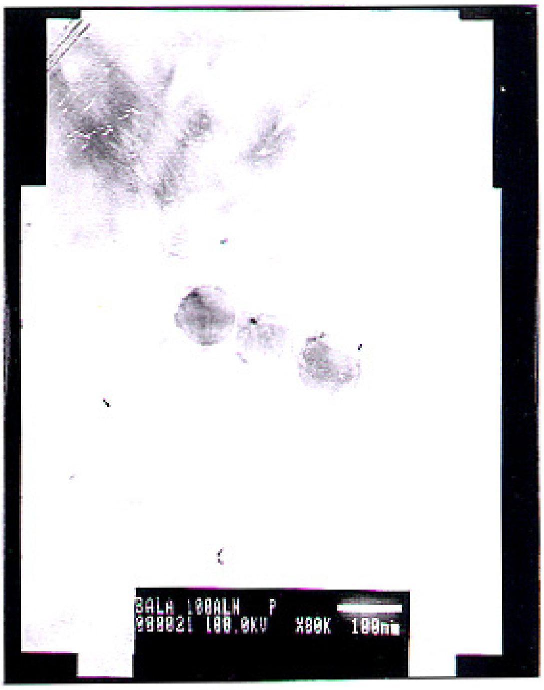
PARTICLE SIZE : 15-40 nm



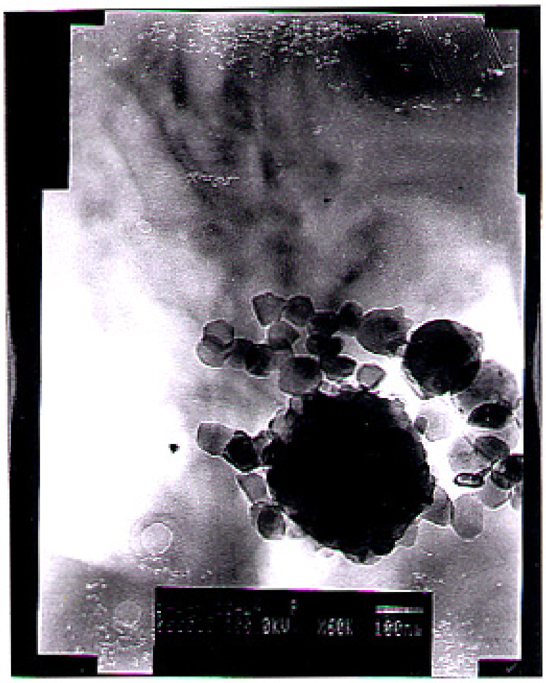
(a)

I = 100A

PARTICE SIZE : ~80nm



(b)



(c)

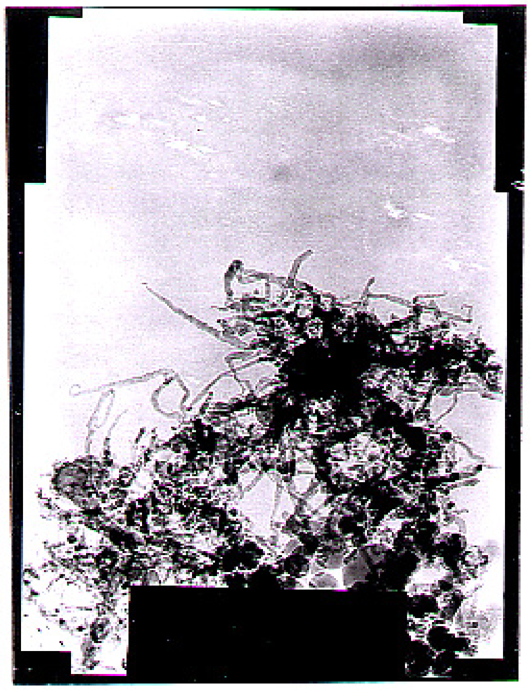
I = 150 A

PARTICLE SIZE :

100- 200 nm

TEM micrographs of AlN nanoparticles synthesised at arc current of (a) 50 A (b) 100 A and (c) 150 A. For arc current of 50 A the particles are perfectly spherical in shape; for 100 A the particles are slightly distorted spherical shape and for 150 A the particles are hexagonal shaped.

Dia : ~ 25-35 nm
length : ~ 500-700 nm



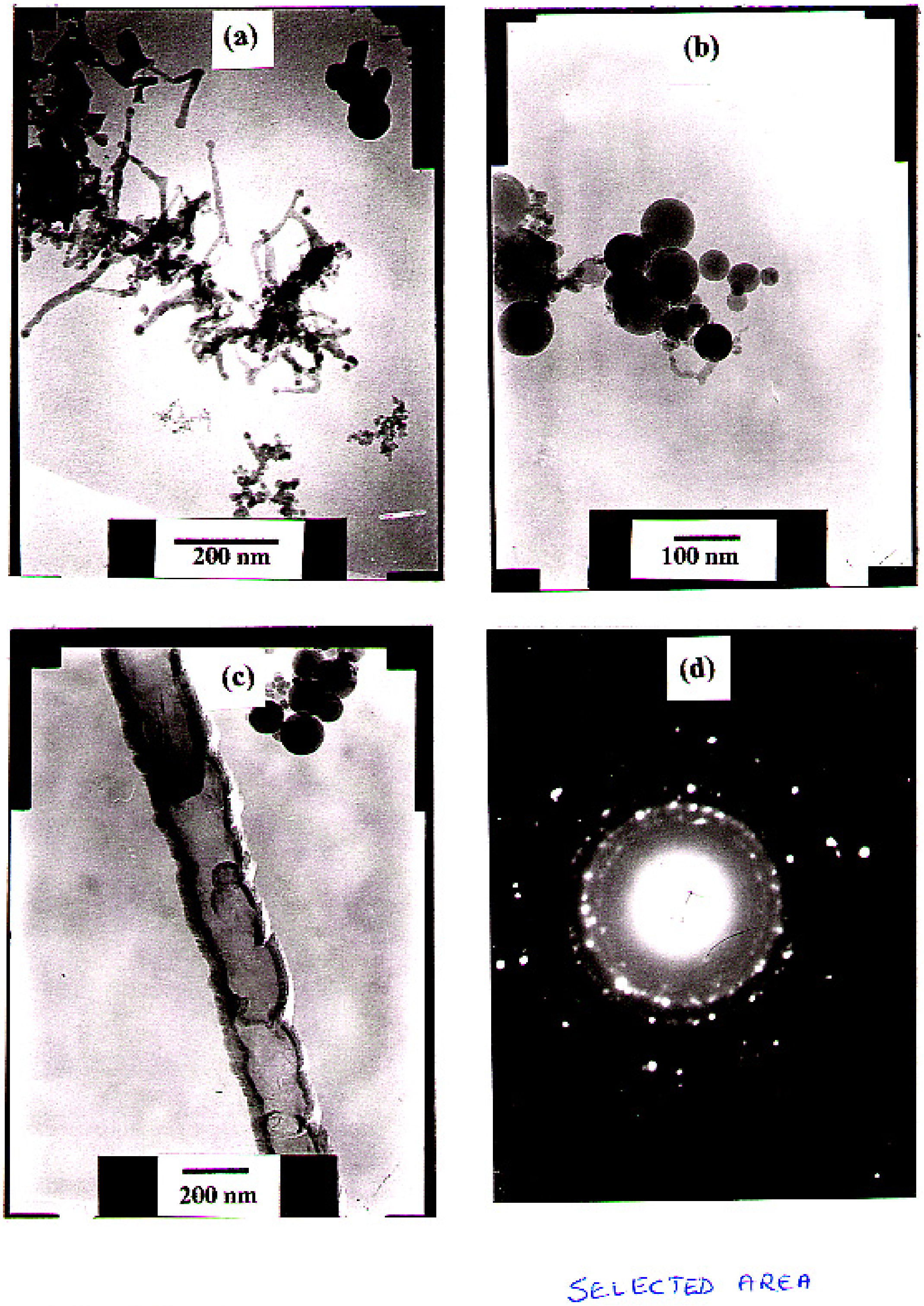
(a)

Dia : ~40 nm
length : ~600 nm

(b)

(c)

Fig. 10 : TEM micrographs of AlN nanotubes and nanoparticles synthesised at arc currents of (a) 50 A (b) 100 A and (c) 150 A. It is seen that for 50 A arc current the nanotube formation is large; for 100 A arc current the nanotube formation is much less and for 150 A there is nanotube formation.



THE BIGGEST SIZE NANOTUBE OBSERVED

SELECTED AREA DIFFRACTION PATTERN

TEM

(a)

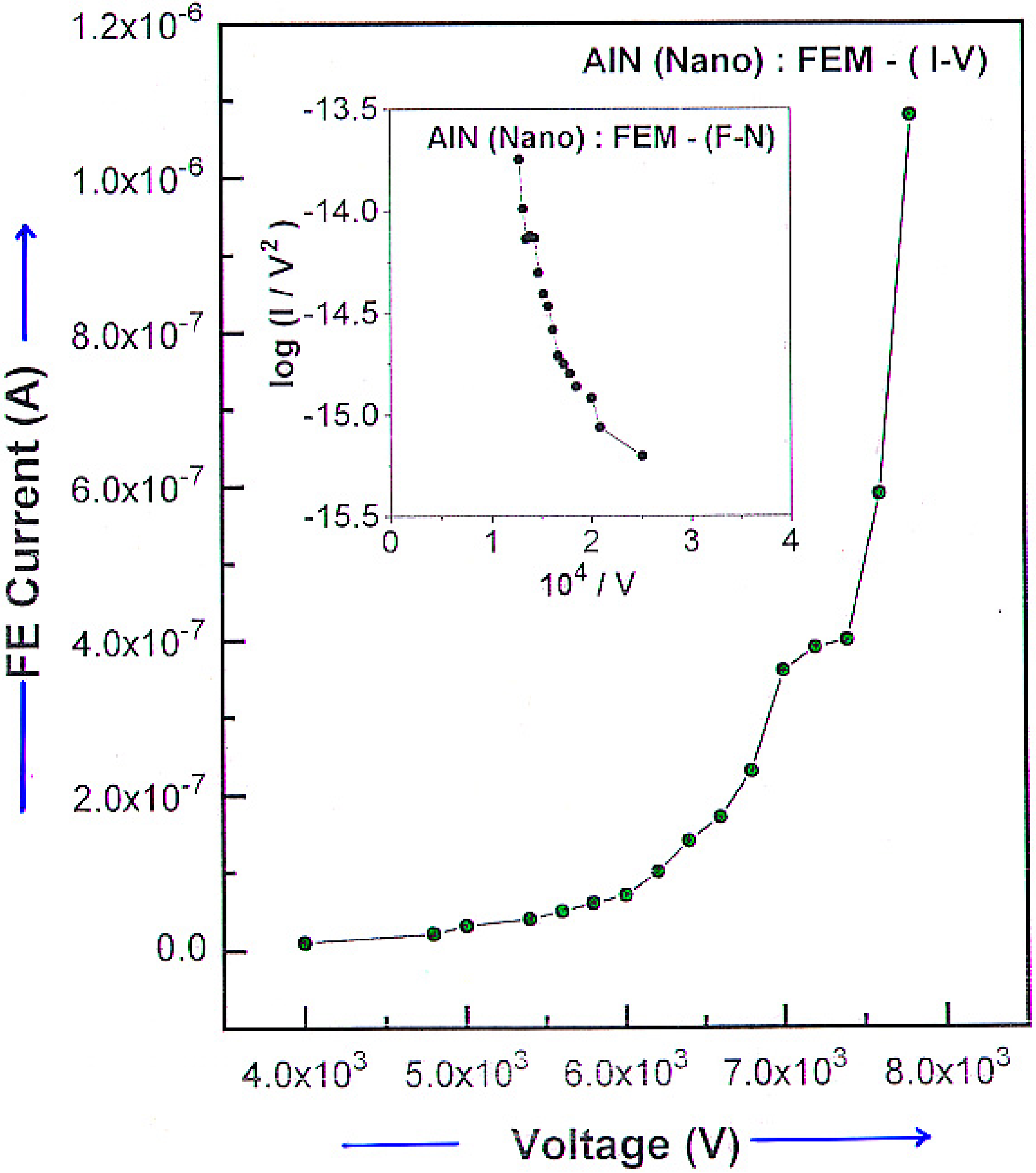
(b)

MAG : ≃ 10^6

SIZE : O·D· = 35 nm

I·D = ~ 20 nm

* Dynamically changing shape
* field 10^7 V/cm
* β (F·E·F) : 75,000



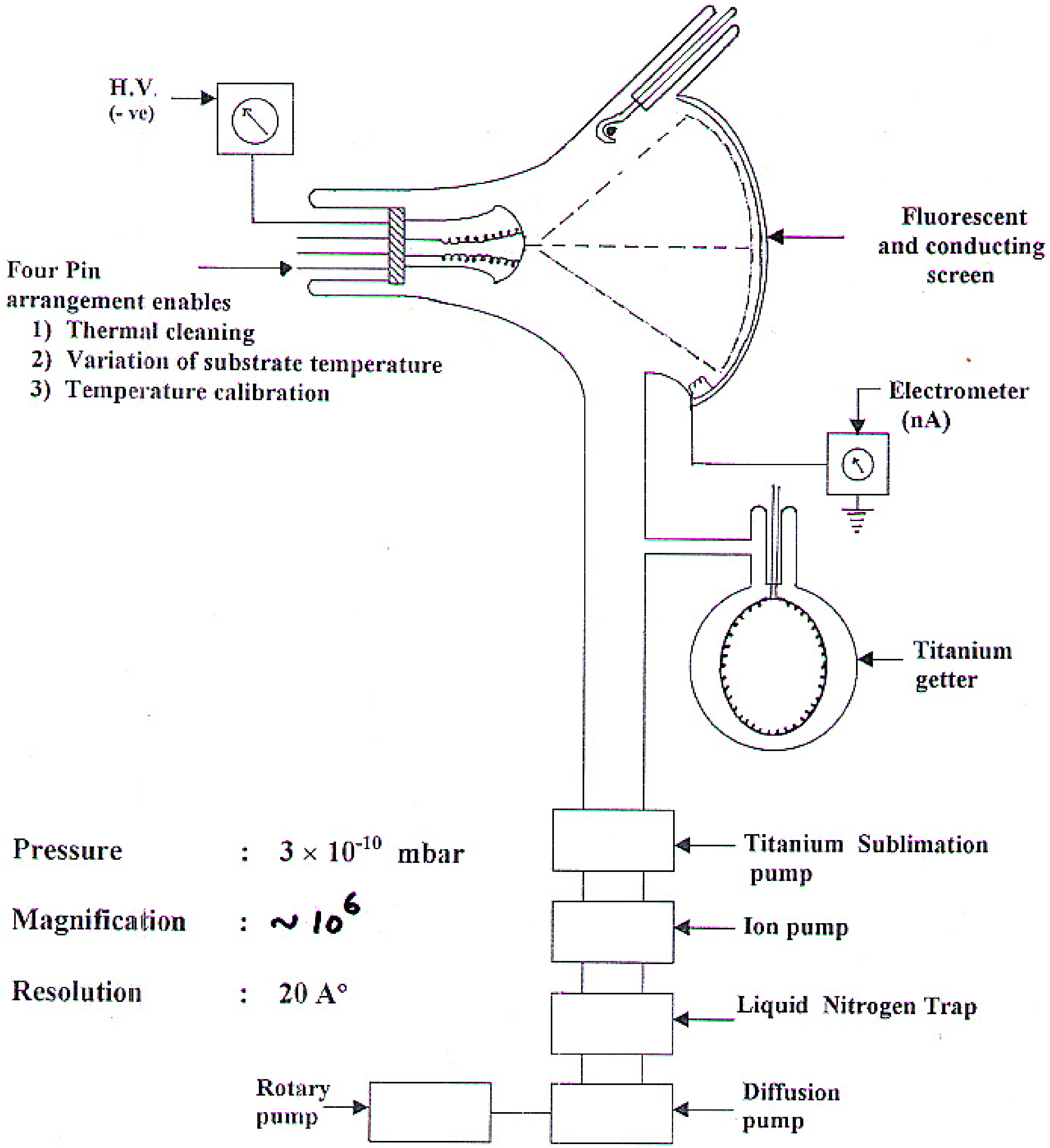
10 nA at 4 kV

1 μA at 7.7 kV

F-N Plot non-linear

⇒ semi insulating nature

Experimental Setup of Field Emission Microscopy



Pressure : 3×10^{-10} mbar

Magnification : $\sim 10^{6}$

Resolution : 20 A°

AlN coated on W wire of 0·1 mm

Tip radius : 0·5 μm

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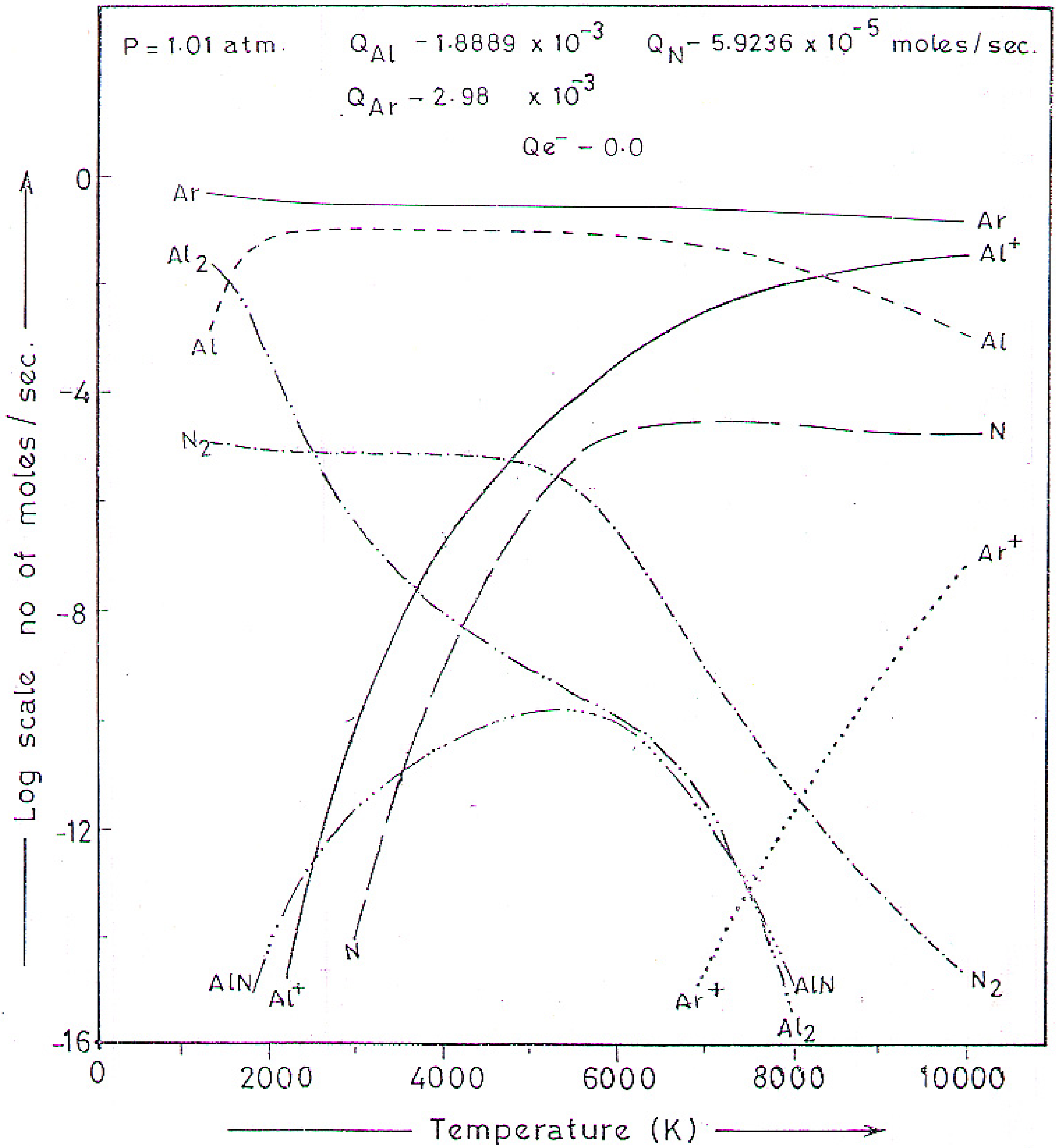
THEORETICAL MODELING

A Fortran code was developed to estimate the concentration of various species that are expected to be present in the arc zone under a given set of temperature, pressure and input elements. This was done by **building a general purpose multi component equilibrium code**. This method is based on the **solution of the non-linear mass action equations coupled to the mass and charge conservation conditions**. **Newton Raphson** technique was used to solve the set of coupled non-linear equations in composition variables.

This programme can currently handle **35 gas and ionized** species formed from 4 elements and electron. The species were divided into basic components, which generated the rest of the other species through chemical reactions amongst themselves.


P = 1.01 atm.
Q Al - 1.8889 x 10-3
Q N - 5.9236 x 10-5 moles/sec.
Q Ar - 2.98 x 10-3
Qe- - 0.0
Ar
Al2
Al
N2
Al+
N
Ar+
AlN
Log scale no of moles / sec.
0
-4
-8
-12
-16
0
2000
4000
6000
8000
10000
Temperature (K)

CONCLUSIONS

- NANO PARTICLES OF ALUMINIUM NITRIDE (Diameter ~ 30 nm) have been Synthesised.

- NANOTUBES (of length 500-700 nm and diameter 30-40 nm) of AlN has been Synthesised for the first time.

- It has been found Possible to Synthesise cubic (metastable) Phase of AlN by the non-equilibrium nature of plasma.

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SEMICONDUCTING AND INSULATING SOLIDS LABORATORY

Group Leader

Prof. Sudha V. Bhoraskar

Members

• Tejashree Bhave • Anisha Gokarna • Prajakta Chaudhari	Semiconducting Solids (Porous Silicon)
• Shilpa Jain • Sanjay Chakane	Conducting Polymers
• Balasubramanian C • Nitin D Sali • Indrani Banerjee	Nanoparticles, Plasma Diagnostics
• Munzer Naddaf	ECR Plasma