Chapter 14
Practicals

14.1 Introduction

In this chapter we shall briefly discuss some easy ways to perform experiments which will enable the beginners to get some experience in the synthesis of nanomaterials and characterization. We shall mention the equipment required and outline the procedure along with some results. These experiments were actually performed in the author's laboratory and are possible to perform in any moderately equipped laboratory without heavy investment.

For chemical synthesis discussed here, simple and inexpensive set of equipment is required. As shown in Fig. 14.1, a multiple neck, round bottom, glass flask can be used. Chemical synthesis reaction is generally carried out under some inert gas (N_2 or Ar) atmosphere to avoid uncontrolled or undesirable oxidation of the nanoparticles by constant flow of the gas in the round bottom flask. Dropwise addition of the reacting solution is carried out. A centrally inserted refluxer in the flask also helps in some cases. One can use other necks for introducing temperature measuring devices (e.g. a thermometer), pH electrode, gas insertion device etc.

After preparing the appropriate precursor solutions by proper weighing/measuring and using appropriate volumes of the chemicals, reactions can be carried out following the steps given in the flow charts.

The nanoparticles are usually separated out from the liquids as a precipitate by using a centrifuge (approximately 2,000–3,000 r.p.m. speed). Precipitate should be washed using appropriate solvents like water, acetone, ethanol or methanol to remove unreacted chemicals or byproducts. Precipitate can be then dried to get sample in the form of powder.

Characterization of samples can be done using some of the techniques given below. The basic principles of characterization techniques were discussed in Chap. 7. All these techniques may not be available/required for high quality research but sometimes observation of colour change and techniques like optical absorption spectroscopy and X-ray diffraction are good enough to indicate the formation

S.K. Kulkarni, *Nanotechnology: Principles and Practices*,
DOI 10.1007/978-3-319-09171-6_14

Fig. 14.1 A typical set-up for synthesizing nanoparticles by chemical method

of nanomaterials. Transmission Electron Microscope (TEM), Scanning Electron Microscope (SEM), and photoluminescence are further useful techniques available at many places.

Usually for optical absorption investigations, nanoparticle sample dispersed in a liquid is used. For transmission or scanning electron microscopy (TEM or SEM) or other microscopies a drop of liquid is placed on suitable grid or substrate and liquid is allowed to evaporate before the measurements are carried out. In some other analysis like photoluminescence, X-ray diffraction (XRD) powder samples are preferred.

It may be noted that the following procedures are only illustrative and only to give one a flavour of nanotechnology experiments and are not necessarily the best possible procedures for obtaining particular nanoparticles. One can follow the literature and obtain better materials following some more stringent conditions or procedures.

14.2 Synthesis of Gold/Silver Nanoparticles

Aim: To synthesize metal nanoparticles of gold and silver.

14.2.1 Chemicals

1. Chloro auric acid ($HAuCl_4$) for gold particles
2. Silver nitrate ($AgNO_3$) for silver particles
3. Trisodium citrate ($C_6H_5O_7Na_3$)
4. Double distilled water

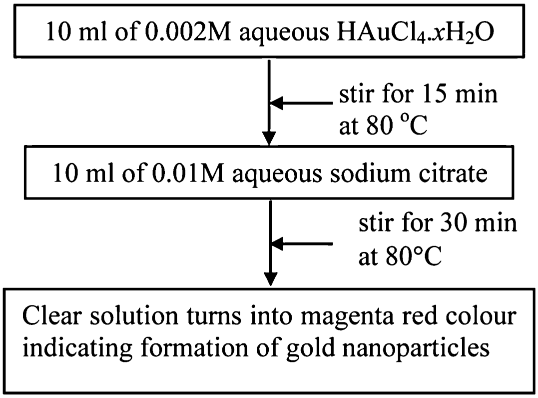
14.2.2 Equipments

1. Round bottom flask
2. Magnetic stirrer cum heater
3. Optical absorption spectrometer (~250–700 nm)

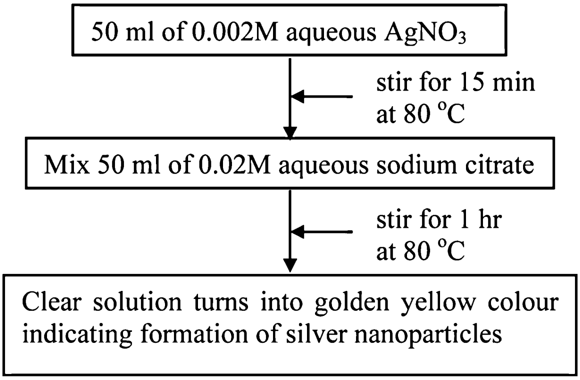
14.2.3 Synthesis Procedure

Procedures of gold and silver nanoparticles synthesis are given in the flow chart form. Synthesis can be carried out using the glass apparatus or set up as shown in Fig. 14.1.

Gold nanoparticles



Silver nanoparticles



14.2.4 Results

The magenta red and yellow colours for gold and silver solutions respectively indicate the formation of nanoparticles. Changing the concentrations, reaction time, temperature etc. one can obtain different shapes/sizes of the particles. This changes the solution colour or shades. There is large literature on these aspects. Typical photograph of gold and silver particles obtained using above procedure are shown in Fig. 14.2a.

Optical absorption spectra can be recorded using a simple absorption spectrometer discussed in Chap. 7. Figure 14.2b illustrates typical spectra obtained for the synthesis described here. It can be seen that peak for silver appears at approximately 396 nm and that for gold at about 530 nm. These are Surface Plasmon Resonance (SPR) peaks discussed earlier.

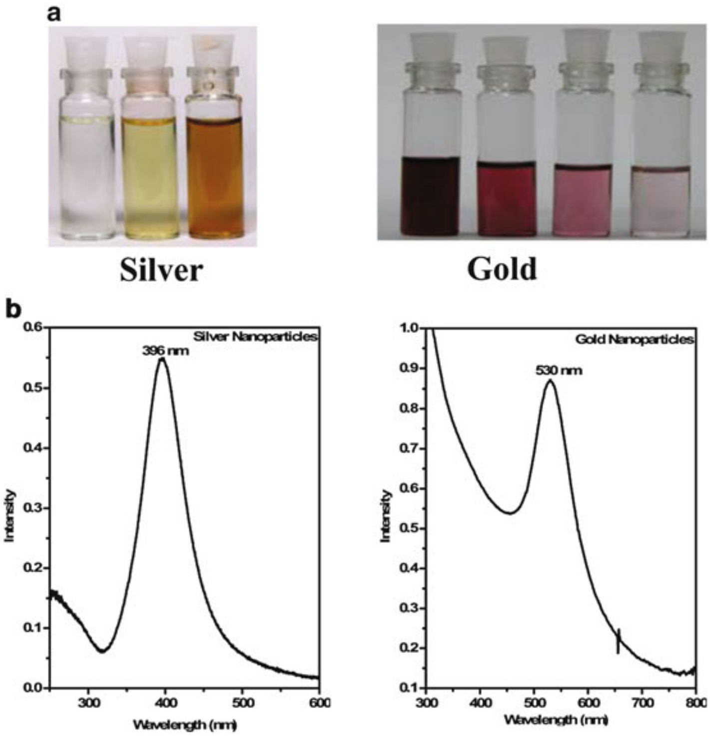


Fig. 14.2 (**a**) Gold and silver nanoparticles in solution. (**b**) Typical absorption spectra of silver and gold nanoparticles

14.3 Synthesis of CdS Nanoparticles

Aim: To synthesize CdS nanoparticles and cap them using thiogylcerol.

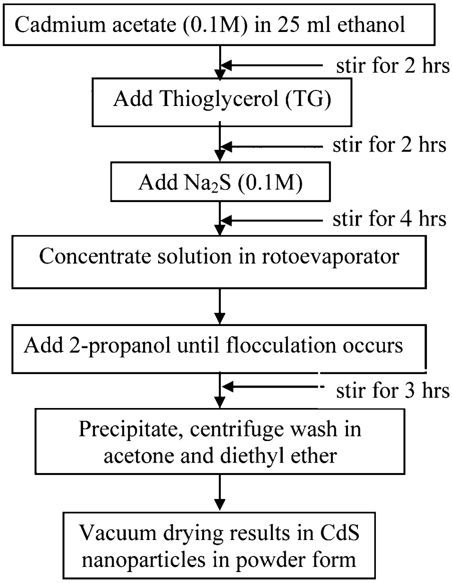
14.3.1 *Chemicals*

1. Cadmium acetate ($((CH_3COO)_2\ Cd\ .\ 2H_2O)$)
2. Thioglycerol ($(HSCH_2CH_2OH)$)
3. Sodium sulphide ((Na_2S))
4. Ethanol

14.3.2 *Equipments*

1. Round bottom flask
2. Magnetic stirrer cum heater
3. Optical absorption spectrometer

14.3.3 *Synthesis Procedure*



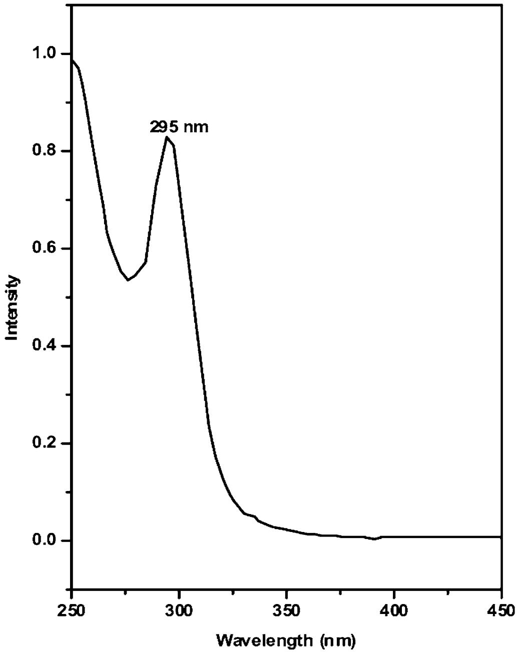


Fig. 14.3 UV-Vis absorption spectrum for CdS nanoparticles

14.3.4 *Results*

As can be seen from Fig. 14.3 an excitonic peak appears at a position much shifted compared to onset of bulk absorption at about 530 nm in case of CdS. Size determination of particles can be carried out using the procedure discussed below for ZnO or TiO_2 nanoparticles. In case of ZnO, procedure using optical absorption is discussed whereas for TiO_2 the XRD analysis is described. One can also obtain ZnS, PbS etc. nanoparticles by similar procedure using different precursors and analyze similarly.

14.4 Synthesis of ZnO Nanoparticles

Aim: To synthesize zinc oxide nanoparticles using a chemical route.

To cap the particles with thioglycerol.

To calculate the size of the synthesized particles using UV-Vis absorption spectrum.

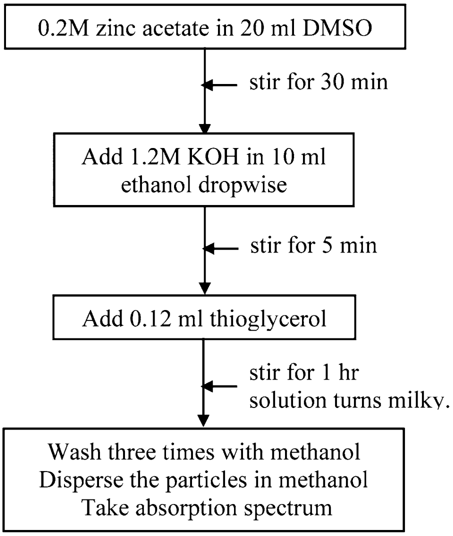
14.4.1 Chemicals

1. Zinc acetate dihydrate ($(CH_3COO)_2$ $Zn.2H_2O$)
2. Potassium hydroxide (KOH)
3. Thioglycerol (TG)
4. Di-methylene sulphoxide (DMSO)
5. Ethanol

14.4.2 Equipment

1. Round bottom flask
2. Magnetic stirrer cum heater
3. Optical absorption spectrometer

14.4.3 Synthesis Procedure



14.4.4 Results

An absorption spectrum as shown in Fig. 14.4 can be obtained. The absorption peak appears at 336 nm.

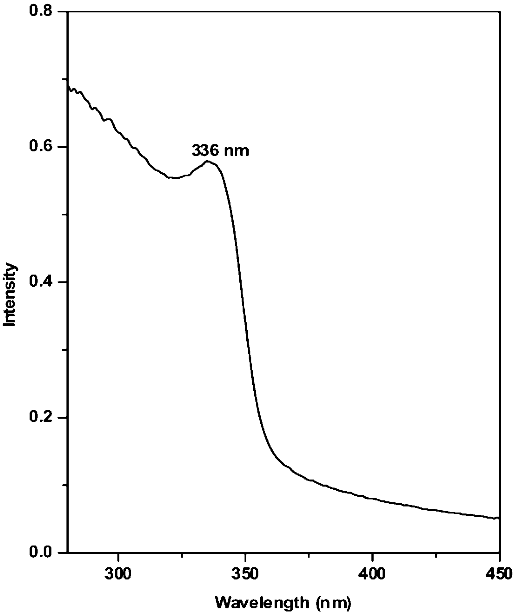


Fig. 14.4 UV-V is absorption spectrum for ZnO nanoparticles

Using the exciton peak position (336 nm) one can determine the energy gap ($E = hc/\lambda$). In this case it is 3.7 eV. This can be used to determine the average particle size using effective mass approximation (or tight banding calculations). Effective mass approximation formula is as follows

$$E = E_g + \frac{\hbar^2\pi^2}{2R^2}\left\{\frac{1}{m_e} + \frac{1}{m_h}\right\} - \frac{1.8e^2}{4\pi\varepsilon_0 R} + \text{smaller term} \qquad (14.1)$$

where, E is band gap of the synthesized particle, E_g – bulk band gap of ZnO (3.3 eV), R – radius of the particle, m_e – effective mass of electron (for ZnO it is 0.28 m_0), m_h – effective mass of hole (for ZnO it is 0.49 m_0), ε – dielectric constant of material (for ZnO it is 9.1), ε_0 – permittivity of free space, and h is Planck's constant $\hbar = h/2\pi$.

The last small term in the Eq. (14.1) can be neglected. Substituting above values in equation, we obtain particle size as 4.6 nm.

14.5 Synthesis of TiO_2 Nanoparticles

Aim: To synthesize titanium dioxide (TiO_2) nanoparticles using a chemical route.

To determine the phase and calculate the size of the synthesized particles using X-ray diffraction (using Scherrer formula).

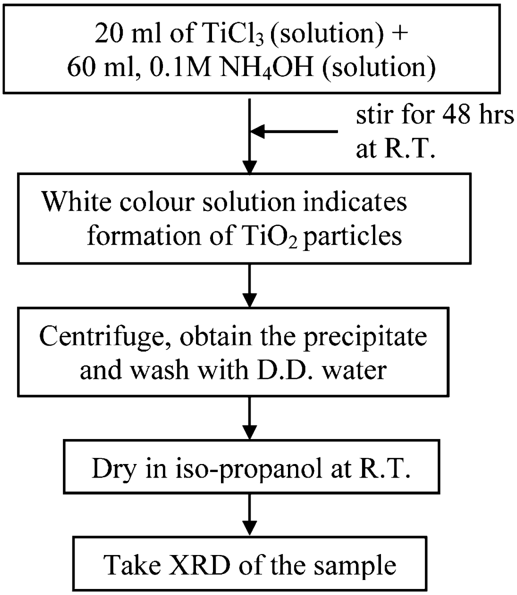
14.5.1 Chemicals

1. Titanium trichloride ($TiCl_3$)
2. Ammonium hydroxide (NH_4OH)
3. 2-propanol ($(CH_3)_2CHOH$)
4. Double distilled (D.D.) water

14.5.2 Equipment

1. Round bottom flask
2. Magnetic stirrer cum heater
3. Optical absorption spectrometer

14.5.3 Synthesis Procedure



14.5.4 Results

A typical diffraction pattern of dry powder sample obtained using CuKα radiation ($\lambda = 0.154$ nm) appears as shown in Fig. 14.5. Comparing with JCPD card no

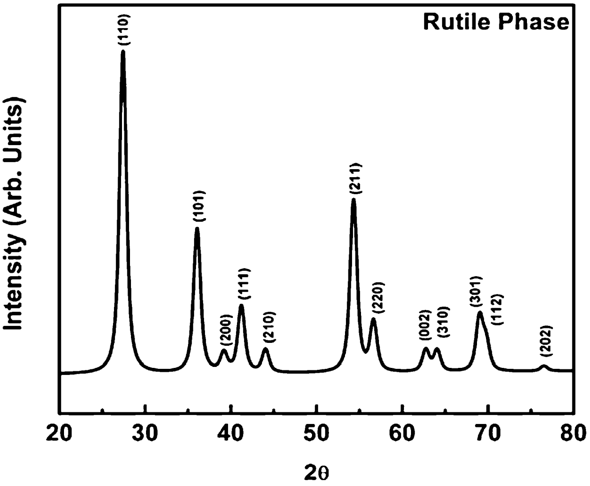


Fig. 14.5 The X-ray diffraction pattern of TiO_2

21-1276, it was found that the particles are in rutile phase. The various peaks are identified with different planes. One can determine the particle size using Scherrer formula as

$$d = \frac{0.9\lambda}{\beta \cos \theta_B} \tag{14.2}$$

where, d is particle diameter, λ – wavelength of X-rays, β – full width at half maximum (FWHM) of diffraction peak, and θ_B is Bragg diffraction peak angle.

The size of the particles as calculated using Scherrer formula turns out to be ~7 nm in this case.

14.6 Synthesis of Fe_2O_3 Nanoparticles

Aim: To synthesize iron oxide particles of different shapes.

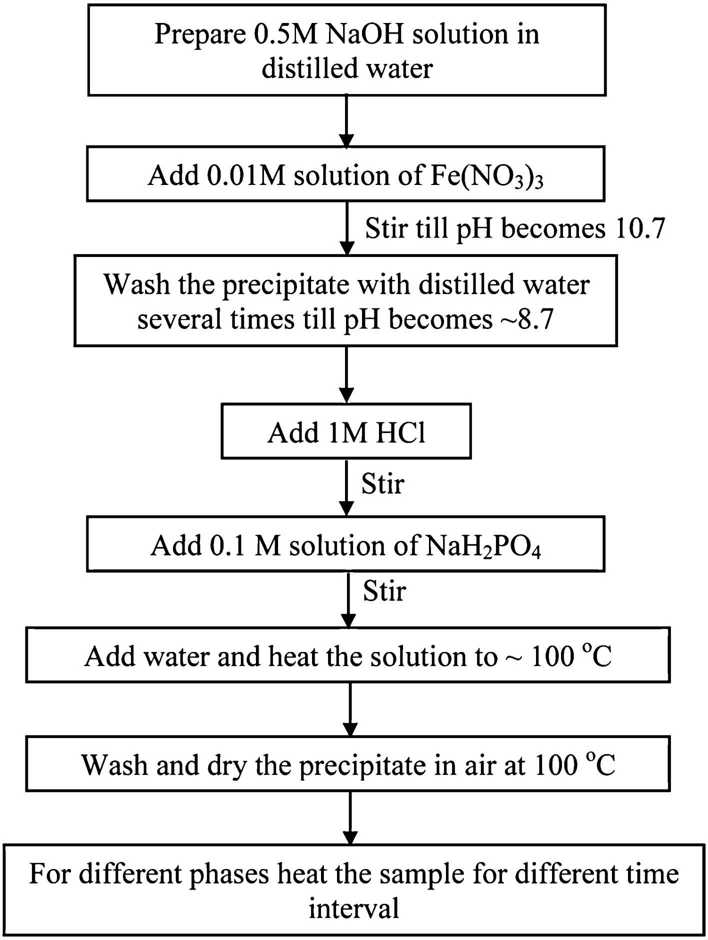
14.6.1 Chemicals

1. Sodium hydroxide (NaOH)
2. Iron chloride ($FeCl_3$)
3. Sodium hexametaphosphate (NaH_2PO_4)
4. Double distilled water

14.6.2 Equipment

1. Round bottom flask
2. Magnetic stirrer cum heater

14.6.3 Synthesis Procedure



14.6.4 Results

In this case different shapes of Fe_2O_3 particles are obtained (Fig. 14.6). X-ray diffraction analysis can be carried out to determine phase. It will be found that these

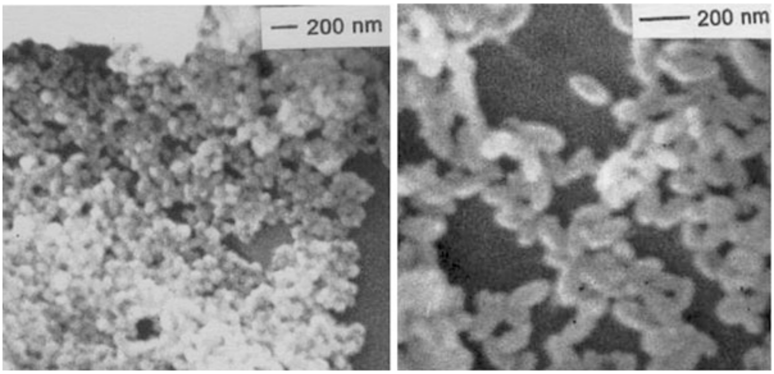


Fig. 14.6 SEM images of Fe_2O_3 nanostructures

particles can be converted into magnetic particles by annealing them in H_2 gas at 350–370 °C for 2 h. The α-Fe_2O_3 particles convert into γ-Fe_2O_3 without substantial change of particle size. Note that here particles have $\sim$200 nm size. However by changing the reaction conditions, smaller particles can be synthesized.

14.7 Synthesis of Porous Silicon

Aim: To obtain porous silicon and study its photoluminescence.

14.7.1 Materials

1. Silicon substrate (p-type) as anode
2. Graphite or platinum electrode as cathode
3. Hydrofluoric acid (48 %)
4. Ethanol, acetone and distilled water for cleaning substrates

14.7.2 Equipment

1. Teflon holder for electrochemical etching of substrate.
2. Voltmeter and ammeter for adjusting voltage and current.
3. Power supply (24 V, 30 mA)
4. Electrochemical cell (teflon or plastic) (Fig. 14.7)

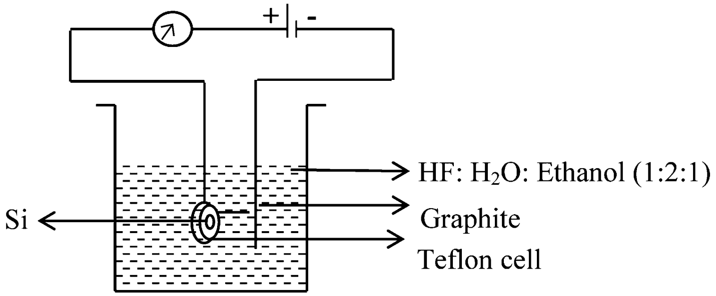
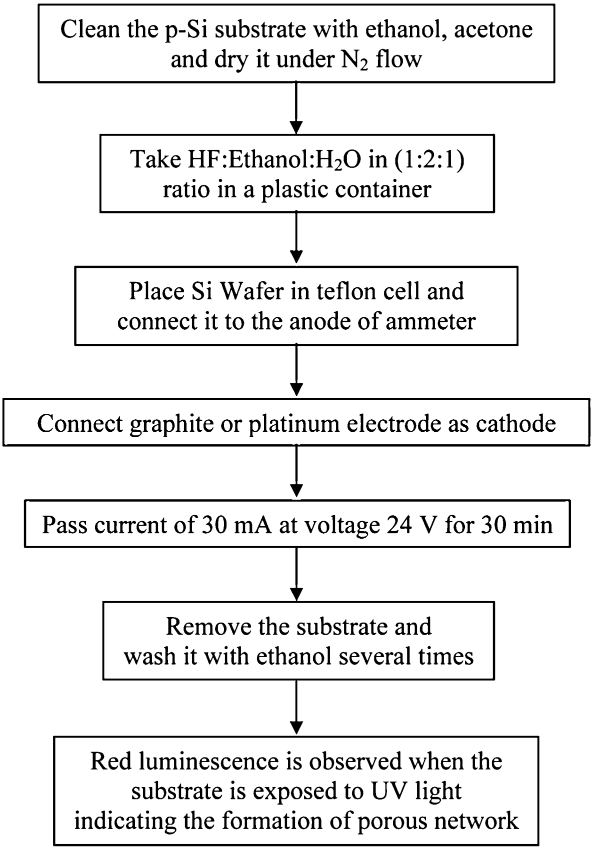


Fig. 14.7 Experimental set-up for porous silicon formation

14.7.3 Experimental Procedure



Clean the p-Si substrate with ethanol, acetone and dry it under N_2 flow

Take HF:Ethanol:H_2O in (1:2:1) ratio in a plastic container

Place Si Wafer in teflon cell and connect it to the anode of ammeter

Connect graphite or platinum electrode as cathode

Pass current of 30 mA at voltage 24 V for 30 min

Remove the substrate and wash it with ethanol several times

Red luminescence is observed when the substrate is exposed to UV light indicating the formation of porous network

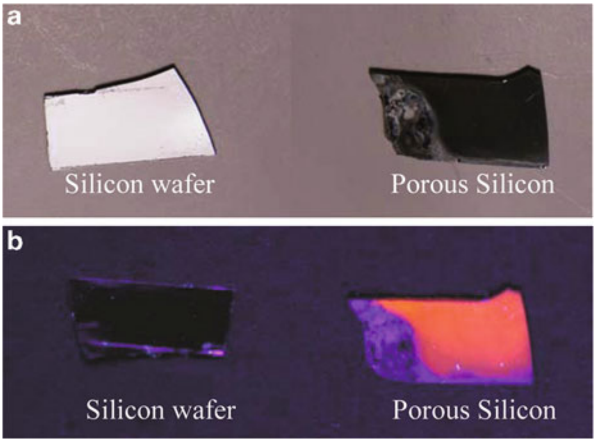


Fig. 14.8 (**a**) Silicon wafer and porous silicon in visible light and (**b**) under UV light

14.7.4 Results

A simple method to check whether silicon has become porous or not, is to just expose the dried sample to a UV radiation. A silicon piece would not show any luminescence but porous silicon glows in the visible range from blue to red colour depending upon the silicon substrate and conditions of the preparation. Figure 14.8 illustrates the photographs of silicon substrate and porous silicon sample prepared under the conditions mentioned above and under UV radiation.

One can also record a luminescence spectrum as illustrated in Fig. 14.9 which clearly shows that there is a broad luminescence band located at about 700 nm in the present case.

If one can inspect the sample under a scanning electron microscope, it will appear porous. However depending upon the substrate and processing of silicon substrate one may get different morphologies of porous silicon. Figure 14.10 illustrates the SEM image of the p-Si substrate used in these experiments.

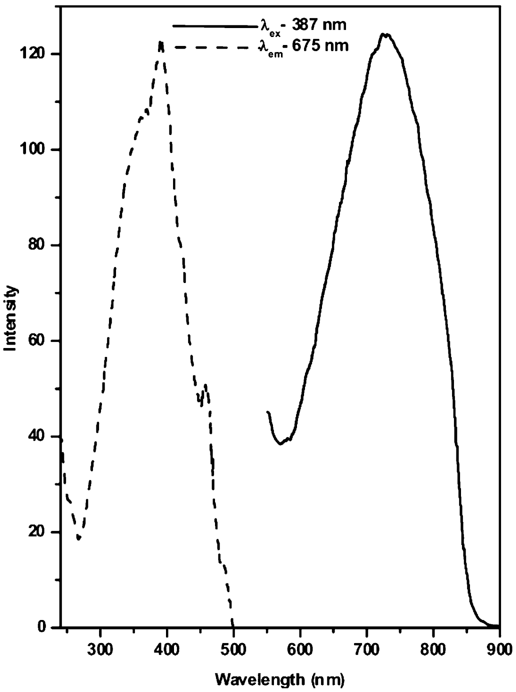
14.8 Introductory Photolithography

14.8.1 Background

Photo-litho-graphy means light-stone-writing in *latin.*

Photolithography is the photographic process to transfer circuit patterns on a semiconductor wafer. This process is useful to fabricate variety of micro components and systems such as electronic circuits, air bag accelerometers, inertial guidance sensors, pressure and flow sensors. Using photolithography a pattern upto

Fig. 14.9 Excitation (- - -) and emission (——) spectra of porous silicon



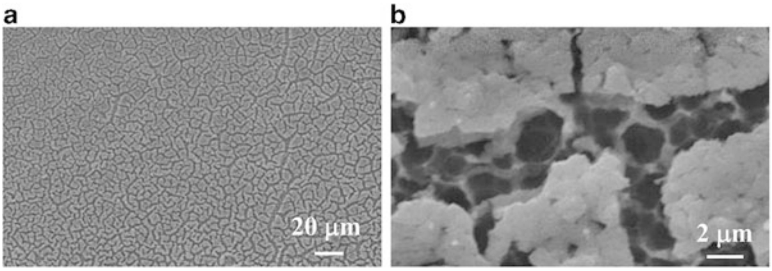


Fig. 14.10 (**a**) SEM image of porous silicon and (**b**) SEM magnified view porous silicon sample in (**a**)

hundreds of nanometer can be prepared on semiconductor surfaces. Size of the pattern is usually in the range of 10–100 μm. Pattern is designed using software such as Autocad. Usually, the designed pattern is bigger and hence is scaled down 100 times. The patterned design of circuit is then printed on a mask (also called as master) in a photography laboratory. Using a single mask, large number of patterns can be generated on semiconductor chips. This is done in various steps such as wafer cleaning, metallization, photosensitive material coating, soft baking, mask

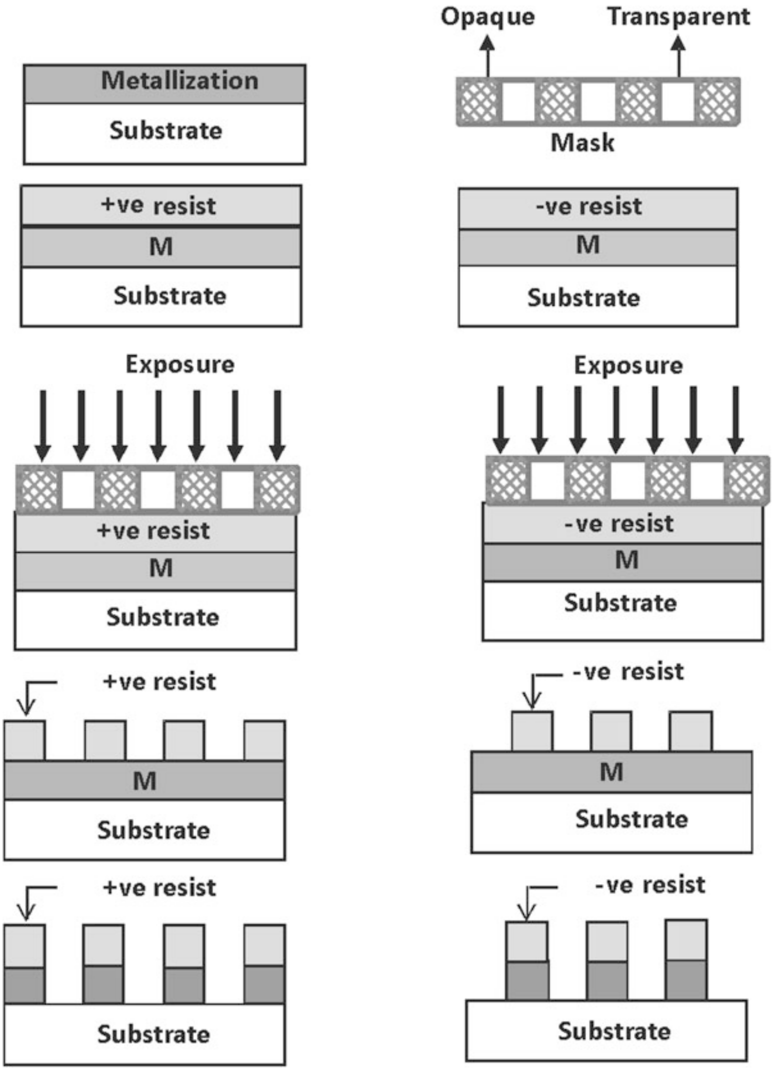


Fig. 14.11 Schematic diagram of photolithography process

alignment, UV exposure, developing, hard baking and etching. Photolithography process for transferring the pattern is shown in Fig. 14.11.

In the first step, the wafer is cleaned chemically to remove organic, ionic and metallic impurities. After cleaning, silicon dioxide which serves as a barrier layer is deposited on the surface of the wafer. Then photoresist is applied to the surface of the wafer. The photoresist material is of two types viz. positive and negative. In positive resists, when UV light is exposed, chemical structure of exposed part of resist changes and becomes soluble in the developer. The exposed resist is then washed away by the developer solution, leaving behind windows of the bare underlying material. Negative resists behave in just the opposite manner. When UV light is exposed to resist, exposed part is polymerized and is difficult to dissolve in developer. Therefore, the negative resist remains on the surface wherever it is exposed, and the developer solution removes only the unexposed portions. These photoresists are generally organic polymers which are sensitive to light. Soft-baking plays critical role because photoresist coatings become photosensitive, or imageable, only after softbaking. Image is transferred from master to substrate by exposing it to UV radiation. Mask consists of clear and opaque areas, which allows exposure of resist material through clear part. Exposure alters the photoresist material chemically and alters its solubility, which is dissolved in suitable solvent called developer. Finally wafer is washed with etching solution to remove the surface not protected by photoresist.

Aim: To transfer the design pattern on given substrate.

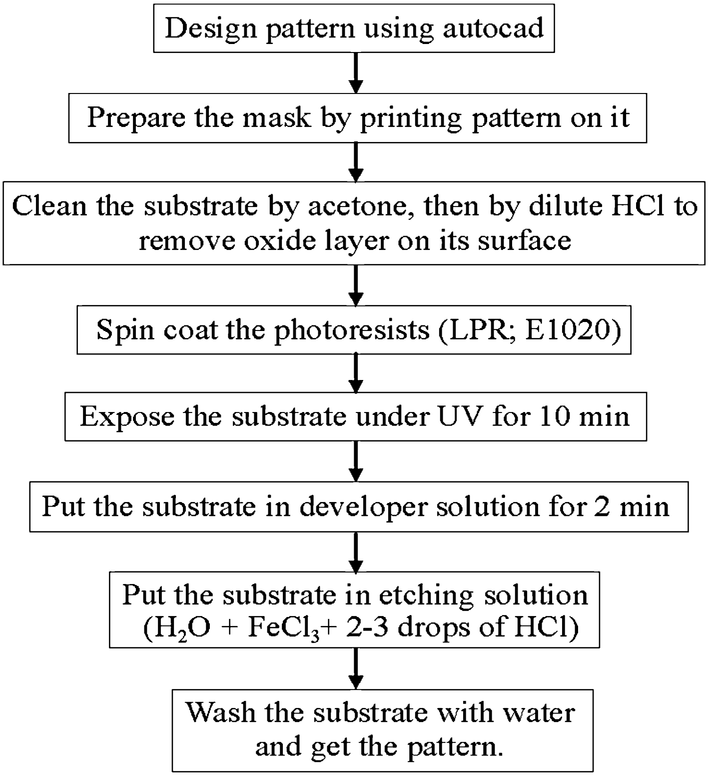
14.8.2 Chemicals

1. Silicon substrate
2. Acetone
3. Negative photoresist (LPR: E1020 of Kodak)
4. Developer (of Kodak)
5. Hydrogen peroxide (H_2O_2)
6. Ferrous chloride ($FeCl_3$)
7. Hydrochloric acid (HCl)

14.8.3 Equipment

1. Spin coating machine
2. UV lamp
3. Autocad software
4. Mask

14.8.4 *Experimental Procedure*



14.9 Introductory Nano (Soft) Lithography Using PDMS

A number of lithography techniques like electron beam, ion beam, X-ray etc. are possible to use in order to pattern nanometric features. However they are too expensive for large scale production. Recently some new techniques have been developed known as *Soft Lithography*. Soft-litho means use of ‘soft materials’ i.e. polymers.

An elastomer of PDMS (poly dimethyl siloxane) of Sylgard 184, Dow Corning is used to prepare microstructures. There are different techniques used in soft lithography: Microcontact printing (μCP), Replica molding (REM), Microtransfer molding (μTM), Micromolding in capillaries (MIMIC), and Solvent assisted micromolding (SAMIM).

This experiment involves synthesis of some micron size particles and then patterning them into small channels using micromolding in capillaries (MIMIC) technique. First we will discuss the synthesis of silica particles.

Aim: To synthesize silica nanoparticles using a chemical route.

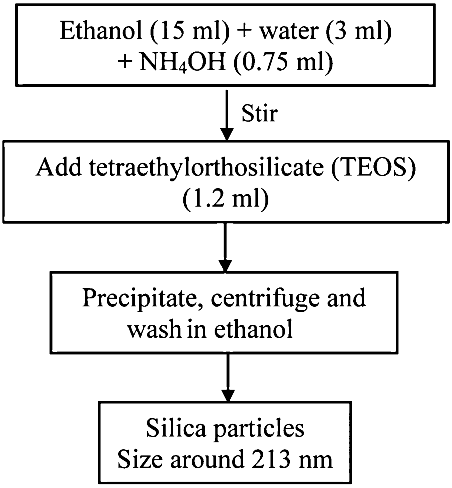
14.9.1 Chemicals

1. Tetraethyl orthosilicate (TEOS) [$Si(OC_2H_5)_4$]
2. Ammonium hydroxide (NH_4OH)
3. Distilled water (H_2O)
4. Ethanol (C_2H_5OH)

14.9.2 Equipment

1. Round bottom flask
2. Magnetic stirrer

14.9.3 Synthesis Procedure



14.9.4 Results

One may record SEM or TEM of the samples just by putting a drop of sample on suitable metal grid (in case of TEM) or substrate for SEM analysis. Here some TEM analysis is shown (Fig. 14.12).

Now we will pattern these particles using *Micromolding in Capillaries* technique. Various steps for the patterning are shown in Fig. 14.13. In this technique, first a PDMS mold is placed on the cleaned substrate (see Chap. 9 for details about

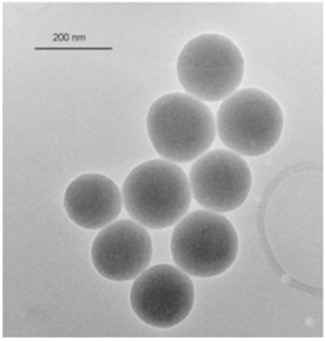


Fig. 14.12 TEM image of silica nanoparticles

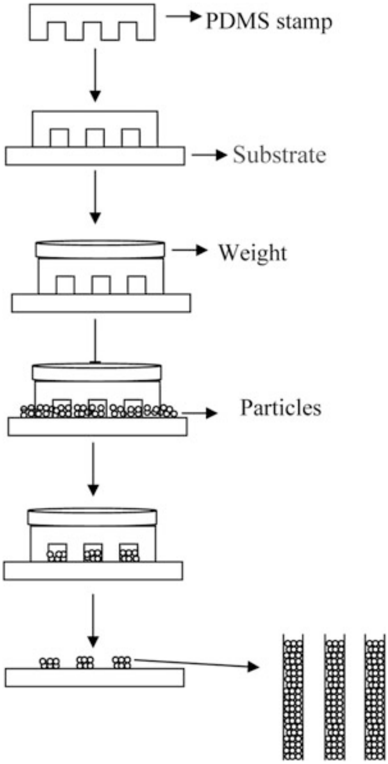


Fig. 14.13 Schematic diagram of micromolding in capillaries technique

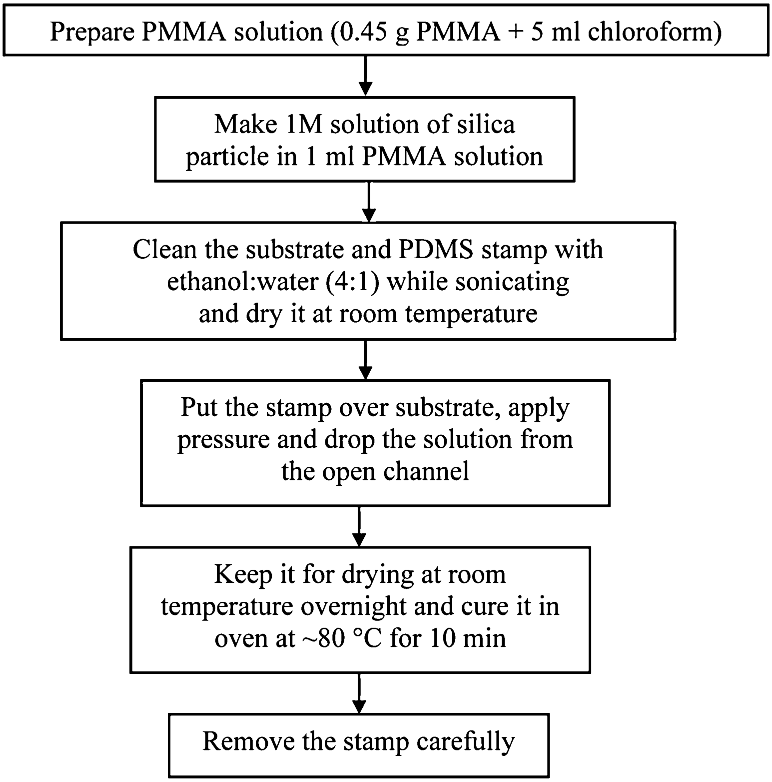
PDMS stamp). Then liquid drop is placed at the open ends of the channel which fills the channels by capillary action. Cure the sample in oven at ~80 °C and remove the stamp carefully. Resulting structures are usually thinner than the height of the groove.

Aim: To pattern silica particles by MIMIC (micromolding in capillary) technique.

14.9.5 Materials and Equipments

1. Silica particles
2. Poly methyl metha acrylate (PMMA)
3. Chloroform ($CHCl_3$)
4. Ethanol (C_2H_5OH)
5. Poly dimethyl siloxene (PDMS) stamp
6. Substrate (silicon wafer or glass)

14.9.6 Experimental Procedure



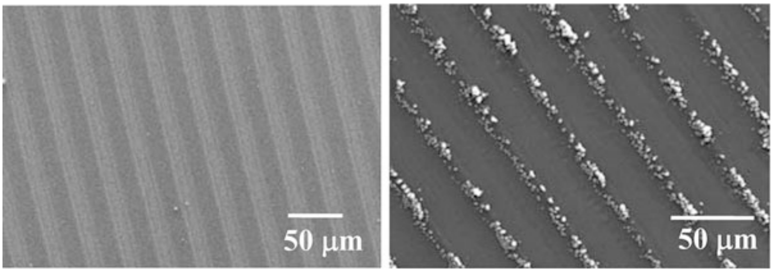


Fig. 14.14 SEM images of (**a**) pattern and (**b**) patterned silica particles

14.9.7 Experimental Set-Up

14.9.8 Results

SEM image (Fig. 14.14) shows (a) PMMA is filled in the grooves of pattern. The groove width is 15 μm and the spacing between the grooves is 10 μm. (b) Pattern of silica particles.

14.10 Fabrication of Porous Alumina or Anodized Alumina (AAO) Template

Aim: To fabricate uniform and ordered pores in alumina using electrochemical method.

14.10.1 Chemicals

1. Oxalic acid
2. Perchloric acid
3. Ethanol
4. Copper chloride
5. Phosphoric acid
6. Methylene orange

14.10.2 Equipment

Electrochemical set up with power supply (see Fig. 14.15)

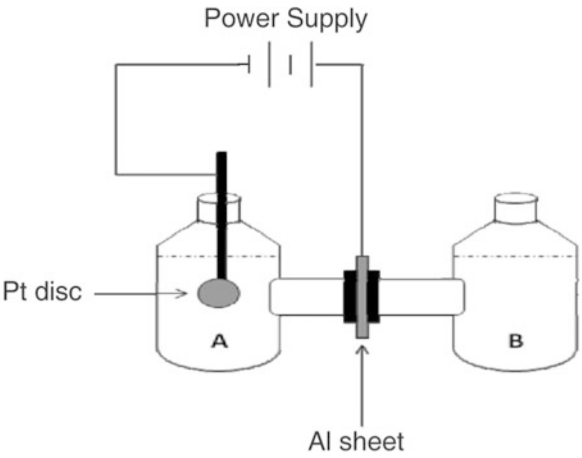


Fig. 14.15 Apparatus for preparation of AAO templates

14.10.3 Fabrication Procedure

Highly ordered porous alumina templates are prepared by a modified two-step anodizing process. Ultrapure aluminum foil (99.99 %) is used.

1. Cut the aluminum foil into 7.5 cm × 4.5 cm sheets.
2. Etch the aluminum sheets in alkaline solution for 2 min and then rinse with ethanol, dry and anneal at 450 °C for 4 h.
3. *Electropolishing:* Aluminum sheet is used as anode and platinum plate as cathode. 1:4 mixture of perchloric acid ($HClO_4$) and ethanol is used as the electrolyte. This solution is kept in a beaker. The electrolysis is done for one minute at the operating voltage of 18 V.
4. *First oxidation process:* Parameters for first anodization process are as follows:

   Anode: Aluminum sheet
   Cathode: Pt
   Electrolyte: Oxalic acid in bottle A and Millipore water in the bottle B. Pt disc is placed in the oxalic acid solution (bottle A) and Al sheet is fixed between the two bottles as shown in Fig. 14.15.
   Voltage: 50 V
   Current: 0.03 and 0.07 Amp
   Time: 1.5 h

5. *Reduction process:* Remove the platinum electrode from oxalic acid. Remove oxalic acid from the bottle and rinse the bottles with Millipore water. Let the Al sheet remain fixed between the two bottles. Place a mixture of chromic acid (1.8 wt%) and phosphoric acid (6 wt%) in bottle A and Millipore water in bottle B. This process is called as reduction process and is used to remove the oxide layer from the surface so that the inside part of alumina sheet can be made porous. The bottles are kept in water bath at 60 °C for 2 h.

6. *Second oxidation step:* Repeat the oxidation process with the same parameter as in Step 4.
7. *Removal of alumina from the other side of the sheet:* Put saturated solution of copper chloride in the bottle B and Millipore water in bottle A. Wait for 1 min. The surface of the template sheet should be carefully watched through bottle A. Once the 75 % of the exposed portion of the template turns black, remove the solutions immediately from the bottles. This step is very critical and should be done very carefully. If the copper chloride solution is allowed to remain in the solution for long time, it will lead to breakage of template. This procedure removes residual alumina from the other side of the AAO sheet. After slowly rinsing the template sheet and bottles with Millipore water, it is observed that the sheet has become translucent.
8. *Pore widening at the bottom of the AAO template:* Put 5 % H_3PO_4 solution in bottle B to open the bottom pore of anodic alumina membrane and dilute aqueous methylene orange solution in bottle A. The bottles are kept until half of the solution in bottle A turns red. Then the template is carefully removed and rinsed with Millipore water. Let the template remain in a beaker containing Millipore water overnight and remove it from water next day.

14.10.4 Results

Typical pore structure obtained using above procedure is depicted in Fig. 14.16. The images are obtained using a scanning electron microscope. Optimization of the parameters and solution concentrations can be made in order to vary the pore size and control the ordered structure. Such pores can be used to deposit different materials in them and obtain 1-D nanomaterials.

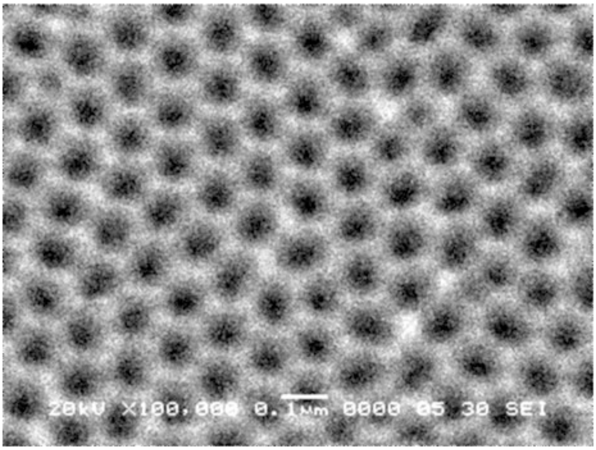


Fig. 14.16 SEM image of AAO template

Further Reading

A.G. Cullis, L.T. Canham, P.D.J. Calcott, The structural and luminescence properties of porous silicon. J. App. Phys. **82**(3), 909 (1997)

B.D. Gates, Q. Xu, J.C. Love, D.B. Wolfe, G.M. Whitesides, Unconventional nanofabrication. Ann. Rev. Mater. Res. **34**, 339 (2004)

S. Link, M.A. El-Sayed, Optical properties and ultrafast dynamics of metallic nanocrystals. Ann. Rev. Phys. Chem. **54**, 331 (2003)

O. Masala, R. Sheshadri, Synthesis routes for large volumes of nanoparticles. Ann. Rev. Mater. Sci. **34**, 41 (2004)

C.B. Murray, C.R. Kagan, M.G. Bawendi, Synthesis and characterization of monodisperse nanocrystals and close-packed nanocrystal assemblies. Ann. Rev. Mat. Sci. **30**, 545 (2000)