इलेक्ट्रॉनिक पदार्थ

ELECTRONIC MATERIALS
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इलेक्ट्रॉनिक सामग्री का विकास पिछले बहुत से वर्षों में एन.पी.एल. का महत्वपूर्ण क्षेत्र रहा है क्योंकि यह विकास अर्कें नई युगित्यों और सिस्टम्स के बनाने में सफल होने को सुनिश्चित करता है। परम्परा एलोक्यों में धार्मिक घराने के लिए जा रहा है जहाँ एन.पी.एल. ने कुछ अग्रणियों अवसर बनाया है और विशेषज्ञता की है। मोटे तौर पर वे विशेषज्ञता इस प्रकार है—

- कार्यनीति अनुप्रयोगों और दोहरा प्रयोग भी जैसे लांग डिके फायस्फोरस। हाल का विकास नैनोसामग्री पर आधारित फॉक्सफोरस है।
- डिवाइसिजन, फोटोनिक्स (W DM & O ASSLM), ट्रीबायोलॉजिकल अनुप्रयोग (एप्लिकेशन्स) (DLC, DLN, C-BN etc.), संयोजी अनुप्रयोग (a-si: He alloys) को प्रदर्शित करने के लिए संगत तत्व फिल्म प्रौद्योगिकियों।
- विकिरण डिटेक्टरों के लिए थोक रूप में सिलिकॉन, घट तथा मेम्स द्रुमांड्र अनुप्रयोग।
- दोरस सिलिकॉन और नैनोस्कलर्ड पोर्स्ट एलुमिना टेंपलेट्स, अर्धचालक नैनोक्रिस्टल और चुम्बकीय बूझार।
- लम्बी लैंच टेप्स के लिए उच्चताप सुपरकंडक्टर्स, विशेषकर प्रदूषण नियंत्रण के लिए सेव्राय।
- लम्बे क्षेत्र की इलेक्ट्रॉनिक बिन्डोज्ड द्रुमांड्र बिन्डोज्ड्रूक्स के लिए इलेक्ट्रोड्मांड्रिजिटेड ट्यूस्टिक ऑक्साइड, पॉलिमरस्रक जैल इलेक्ट्रोड्मांड्राइट्स आदि और इलेक्ट्रॉनिक तथा बॉयॉटेनोलॉजिकल सूक्ष्म प्रौद्योगिकियों और संबंधित अनुप्रयोगों की विविधता के लिए पॉलीमर को कंडक्ट करना।
Development of Electronic Materials has been an important area of activity at NPL for the last many decades as this development alone ensures success in the fabrication of novel devices and systems. Focus, in recent years, has however shifted to those areas where NPL has been able to create some unique infrastructure and expertise. Broadly speaking they are the following:

- Phosphors for some strategic applications, as also of dual use, such as long decay phosphors. Recent development has been phosphors based on nano-materials.
- Thin Film Technologies relevant to display devices, photonics (WDM & OASLM), tribological applications (DLC, DLN, C-BN etc.), sensor applications (a-Si:H & alloys).
- Silicon in the bulk form for radiation detectors, PV and MEMS applications.
- Porous silicon and nanostructured porous alumina templates, semiconducting nanocrystals and magnetic multilayers.
- High temperature superconductors for long length tapes, specialty ceramic for pollution control.
- Electrodeposited tungstic oxide, polymeric gel electrolytes etc. for large area electrochromic windows (SMART WINDOWS) and conducting polymers for a variety of electronic and biotechnological and related applications.
Luminescent Materials

The synthesis of strontium aluminate based long decay phosphor (LDP) was taken to meet the demand of Defence Laboratory, Jodhpur (DLJ). Initial brightness and decay times are the key features of any long decay phosphor. Therefore, some key processing steps like of heat treatment was carefully controlled to further improve the quality of the phosphor.

Figure 4.1 shows the dependence of decay characteristics and initial brightness as a function of heating rate of firing composition of the phosphor. The best heating rate for optimum brightness and decay has been found to be in the range of 300° - 600° C/hr. Similarly, other parameters like heating time at constant temperature, rate of cooling and atmosphere during firing were also studied. On the basis of feedback from the user agency i.e. DRDO, phosphor characteristics e.g. brightness, decay time, particle size etc. were tailored to meet their specific requirements. Process modification for industrial adaptation, with the aim of cost reduction, environmental pollution, energy saving and process simplification was also carried out.

Long Decay Phosphor developed earlier was also modified to be used as pigment for preparing paints by mixing with suitable paint vehicle. Particle size of the phosphor, transparency, viscosity, chemical inertness to phosphor and adhesion of paint vehicle to substrate were some of the important parameters that had been worked out for deciding formulation of LD Paint.

One kg of LDP powder, one litre of LD paint and 5mx10cm of LDP tape were sent to Defence Laboratory, Jodhpur (DLJ) on 31st August 2001. The photograph of a pilot facility developed to produce such phosphor is given in Fig. 4.2.

Next, on the basis of evaluation report received on small fluorescent screens (4"x4") of gadolinium oxysulfide sent earlier to DLJ, under another sponsored project of DRDO entitled "Development of Luminescent Screens", work on preparation of gadolinium oxysulfide phosphor in bulk quantities and fabrication of larger area (8"x8") fluorescent screens were taken up. A number of samples of Tb/Pr doped gadolinium oxysulfide phosphor with varying amounts of alkali halides were made in significantly large amounts. The thermo-luminescence studies were simultaneously carried out to investigate effect of trapping states present in the system on radiative transitions of activator centers. Figure 4.3 shows effect of Tb concentration on thermal glow curves of Gd₂O₂S samples.

Using these phosphors, development work on trial screens of 8"x8" size were initiated. Some of the screens in pairs were sent to DLJ for further evaluation under x-rays/ gamma rays before batch production for supply to DLJ commenced. Results of acceptance tests are still awaited. Electroluminescent powders, emitting in orange-red and blue colour were also developed for fabricating multi-colour flexible electroluminescent devices under the same project.

Work on development of Nano-phosphors was also initiated. Initial experiments were performed on growth of ZnS particles in nano-scale using some known chemical routes. The existence of nano particles was investigated by SEM and XRD measurements. The formation of ZnS lattice has been confirmed as shown in Fig. 4.4.
Fig. 4.2: Photograph of the Phosphor Pilot Plant at NPL

Fig. 4.3: Glow curves of Gd₂O₂S:Tb with different Tb concentrations
The group have succeeded in reducing the particle size from normal 10 micrometer size of bulk particles to 50 nm. The work is continuing to further reduce it to about 5 nm without agglomeration and loss of desirable luminescence properties.

**Thin Film Technology**

A project funded by Ministry of Information Technology, Govt. of India, entitled “Silica-on-silicon integrated optical devices for wavelength division multiplexing (WDM) applications (Part-I)” was concluded in Dec. 2001. Under this project, the deposition of silica layers several microns thick on silicon substrates by Plasma Enhanced Chemical Vapour Deposition (PECVD), Flame Hydrolysis Deposition (FHD) and electron beam deposition were successfully carried out. Whereas transparent and fairly uniform silica films were deposited by electron beam deposition and PECVD, the films deposited by FHD were not of the desired optical quality and need further development to achieve good quality films. The films were characterized for their refractive index, extinction coefficient and thickness from spectrophotometric measurements of the reflectance vs wavelength, using in-house developed calculation procedures and software. Samples of thick silica films were provided to CEERI, Pilani, the co-investigators of this project, for the fabrication of complete integrated optic devices in silica-on-silicon optical waveguides. Very valuable exposure to state-of-the-art PECVD deposition facilities and film characterisation facilities, as well as some recipes for successful deposition of uniform thick silica films, were gained during visits of NPL scientists to U.K. and the Netherlands, as well as through correspondence with foreign researchers. This knowledge will be valuable for future work in this area, where all technology and knowledge is usually cloaked in commercial secrecy.

Transparent conducting coatings of ITO and high reflectance all-dielectric mirror coatings were deposited by electron beam deposition, and thick amorphous silicon layers were deposited by PECVD, on polished ophthalmic glass substrates, for the fabrication of optically addressed spatial light modulators (OASLM) by the Display Devices group at NPL, as part of an external project funded by IRDE (DRDO). By July 2002, this work should reach its successful conclusion with the fabrication of complete OASLM’s on highly polished fused silica substrates, meeting all the specifications of the sponsors.

Studies were conducted on the modelling of binary composite films for determining the refractive index and extinction coefficient as functions of film composition.

A sophisticated vacuum plasma arc deposition system, indigenously designed and fabricated (as shown in Fig.4.5 ) to grow ta-C (highly tetrahedral amorphous carbon) films became fully functional.

**Design and Development of Large Area PVD Coaters for MgO Deposition for PDP Displays**

This was taken up as a consultancy assignment (contract R&D) for a reputed manufacturer of such displays. The work involved providing design of PVD & PECVD reactors (vacuum evaporation, Magnetron sputtering
Silicon & Silicon Devices

R & D work on development of silicon PIN photodiodes was continued. During the year 2001-02 some shallow junction n+-p-p+ structures of 1 cm x 1 cm size were made on 10 ohm-cm resistivity p-Cz-Si wafers of 50 mm diameter by carrying out B-diffusion at the back using a borosilica film and P- diffusion on the front surface using a solid dopant source. The n+ - front junction had a junction depth of 0.2 µm and the sheet resistivity of the n+ emitter was ~ 95 Ω/□. Front and back contacts were made with vacuum deposited Al metal. The back surface was fully covered but the front contact was in the form of a 0.75 mm wide strip using photolithography. Four PIN photodiodes, each of 1 cm x 1 cm size, made in a 50 mm diameter wafer, are shown in Figure 4.6. The dopant impurity concentration profiles in the n+ front emitters of a photodiode were determined using SIMS and are shown in Fig. 4.7. The figure clearly shows that not only the junction depth (xj) but the front surface concentration of the dopant impurity is also significantly smaller in case of profile 1. It was used for fabrication of the shallow junction n+-p-p+ structures for photodiodes.

I-V characteristics of each photodiode were measured under dark as well as under illumination and PECVD to handle very large area substrates (up to 150 cm diagonal). In case of Magnetron sputtering Mg target was required to move to and fro under a static substrate. Such systems have earlier not been manufactured in the country. NPL provided all the design details and closely interacted with the fabricators of these equipment in the country and helped install the system. In a parallel activity small area MgO coatings were developed in our laboratory and fully characterized to gain first hand experience to support the user industry in its efforts.

High Rate Deposition of a-Si:H and SiO_2 for Photonics and Sensor Application

NPL has been successful in developing many PECVD based processes and equipments in past and such equipment have been supplied to other institutions as well. High rate deposition of a-Si:H for photovoltaic, photonic (OASLM), sensor (radiation detector, color sensing) has also been investigated for some time. In recent past VHF PECVD of SiO_2 was also attempted to see its utility for controlled deposition of thick layers (doped and undoped) for optical waveguide application. For investigating VHF & pulsed VHF processing of amorphous semiconductor and dielectric layers an ambitious project with DST support has since been defended.
previous and after scribing it out from the wafer. The dark current was found to be rather large (in micro ampere range) for small reverse bias (-2V). The studies were planned to determine its cause and to find out ways of reducing it substantially. Spectral responses (SR) of the photodiodes were measured in 400-1100 nm range and compared with that of a typical solar cell made having screen printed contacts. Figure 4.8 depicts the SR curves for a silicon photodiode and a solar cell. In the visible range (400-750 nm) the SR of the photodiode is much superior to that of the solar cell also fabricated at NPL. This is indicative of superior quality of the n+ emitter of the photodiode. High spectral response of the photodiode in the short wavelength range is very important for detection of scintillation raditions emitted by BGO, CWO crystals under excitation by gamma rays which lie in the visible range.

Microstructure Devices

The activity of the group during the year 2001-02 has been focused on nanostructured materials for chemical and magnetic sensors. Other activities include the externally sponsored projects on CdTe passivation of HgCdTe by electrodeposition technique for use in PV FPA’s and the DST Project on Magnetic Multilayers. Significant research results are briefly mentioned below:

Porous Silicon

This is a new activity started to explore the utility of porous silicon as a chemical sensor material. The formation process of porous silicon was optimized. Our process involves deposition of 300 nm Al on Si wafer, 500°C anneal in Ar for 10 min, anodization in an electrolyte consisting of HF and H₂O₂ in a 2:1 ratio by volume at a current density of 30-50 mA/cm² for 10-30 min. A strong photoluminescence signal was detected in the wavelength region of 500-750 nm with a peak at about 650 nm. Quenching under laser illumination at 10 mW has been observed and studied in depth. To stabilize the porous silicon surface, PSi nanoparticles (PSN's) separated mechanically from the wafer were embedded in polymers. On embedding in PMMA, complete absence of quenching was observed. In optically transparent NOA85, quenching and recovery was repeatedly observed. Time dependence
studies showed that $\tau_{\text{Recovery}} \gg \tau_{\text{quenching}}$. Porous silicon stabilization by acetylene exposure was also studied. Low temperature optical illumination during acetylene exposure leads to quenching followed by recovery of the peak at 650 nm. High temperature thermal reaction however leads to quenching followed by recovery with a peak at 580 nm. Lowering of nanocrystal size is responsible for these results. This is confirmed by FTIR studies which show complete replacement of Si-H bonding, formation of four membered Si-C=C-Si rings during optical reaction and penetration of C into PSi in the case of thermal reaction. Electrodeposition of CdTe in porous silicon was also studied. Cyclic voltametry was used to determine deposition potential for CdTe electrodeposited in nanopores. FTIR investigations and I-V and C-V studies were performed. Non linear I-V relationship indicates barrier formation.

**Nanostructured Porous Alumina Templates**

A new activity for the preparation of nanostructured porous alumina templates by a simple anodization process was initiated. This would enable the study of an array of nanowires of semiconducting materials for photoelectronic and sensor applications. Optimization of anodization was performed using (I) Aluminium sheet and (II) Al film thermally deposited on Si wafers. Porous films with 20-40 nm pores were formed. Incorporation of compound semiconductors and oxides in these pores is being investigated. Bismuth Molybdate Ethanol Sensor material was investigated for possible incorporation in the nanostructured templates. Thin/thick film preparation was investigated. Sol gel process was also investigated. Films were prepared using hexanoate precursor. XRD, IR studies confirm single phase formation. The response time to ethanol was $\tau \approx 2$ sec which decreases with film thickness. These results show an improvement compared to ceramic processing where mixed phase formation and long time constants are observed. Highest sensitivity is obtained with the beta phase. The effect of additives such as Sb$_2$O$_5$, TiO$_2$ was also studied.

**Semiconducting Nanocrystals in Insulating Matrix**

This activity has been continued and studies on CdS, CdSe and CdTe in TiO$_2$ and SiO$_2$ were undertaken. Nonlinear optical properties and quantum confinement effects were observed in RF sputtered films. Post deposition anneal to 300 °C has been shown to lead to Cd vacancies and surface effects. Optimization of parameters such as Ar pressure, RF power, temperature of deposition was performed. It has been shown that Cd concentration is critical for the formation of stress free films of high conductivity. The current transport mechanism has been shown to be space charge limited and mediated by Cd-vacancies. The peak in current is related to Cd vacancies.
**Magnetic Materials**

As part of the DST sponsored project on development of multilayer magnetic materials for sensor applications, multilayers of Co/Ag were deposited. The total structure including capping layers of Ti is represented by Ti(5nm)[Co(1nm)/Ag(4nm)]_35Ti(5nm). This stack of 35 alternating layers of Co and Ag was subjected to 300-350°C anneal for formation of a discontinuous multilayer structure. XRD SEM studies confirm that (111) oriented growth has taken place. VSM studies indicate ferromagnetic coupling in layers. Moderate Magnetoresistance (MR) has been observed at 3500 Oe. Lithium Ferrite Nanoparticles were also investigated for possible ferrofluid applications. Lithium ferrite nanoparticle synthesis was achieved using citrate precursor. XRD, IR studies confirm single phase lithium ferrite formation. Disordered α-LiFe₅O₈ is observed at 200°C and an ordered β-LiFe₅O₈ at 350°C. Magnetic properties are found to be suitable for ferrofluid applications. Microwave processing of Ni-ferrite nanoparticles was investigated. The Ni ferrite nanoparticle synthesis was performed using citrate precursor. Comparison of conventional and microwave processing showed that microwave processing results in superior product.

**Electrodeposited Polycrystalline Compound Semiconductors.**

This is an established activity and earlier a sponsored project from MNES was undertaken to develop CdTe solar cells. Attempts were made to vary the band gap and lattice parameters to produce superior films for photovoltaic and related applications.

Electrodeposition, pulsed electrodeposition, chemical bath deposition and spray pyrolysis were all investigated for the formation of ternary compounds based on CdTe. Electrodeposition process was optimized for the formation of CdPbTe, CdBiTe, CdSnTe, and CdSbTe. EDX, SEM, XRD, optical bandgap and IR absorption studies were performed on these films. One of the interesting results is the formation of highly conducting CdInTe₂ by simultaneous electrodeposition. It was observed that optical band gap E₉ 1.2 eV is obtained at a cathode potential of ~0.5 V in contrast to 1.1 eV at -0.54 V. As part of the externally sponsored project, CdTe passivation of HgCdTe by electrodeposition technique for use in PV FPA’s: a feasibility study, CdTe electrodeposition over MCT was investigated. Chemomechanical etching & polishing of MCT was necessary and the conditions optimized by using cyclic voltametry studies. CdTe electrodeposition was performed at both room temperature and 50°C. Thickness and growth rate were optimized. XRD confirms cubic CdTe phase formation. XPS confirms absence of Hg on surface. MIS fabrication and C-V measurements are in progress. Alternate approaches for passivation were investigated. These included formation of Double layer CdS/ CdTe and ZnTe.

**Superconducting & Ceramic Materials**

**Special Ceramics and Superconducting Tapes**

This group has been engaged in the development of long length tapes of Bi based HTS compounds and exploring a new concept in high current transport.

Efforts have been focused on the development of process technology of Bi₁.₈₄Pb₀.₄Sr₂Ca₂₂Cu₃O₁₀₊ₓ : 10 wt% Ag (an optimum value) high temperature superconductor (HTS). This is aimed at producing reproducibly, (i) HTS magnet for (high magnetic fields) at relatively high temperature and also for low loss high electrical power transport (Ic) at, 77K, in long length multifilamentary tapes, and (ii) high Ic values at 77K in Bi - 2223 tubes/rods as current leads for cryogen free cryo-cooled superconducting magnet.

A significant achievement in this direction has been realizing 25 meters long Bi-2223 Ag clad multifilamentary (32 filaments) tape, which is then translated into spool form required for winding small prototype magnets. The preliminary studies showed that tape in spool form is end-to-end superconducting, having
reproducible $J_c$ value of order of $10^4 \text{A/cm}^2$ at 77K and $\sim 10^6 \text{A/cm}^2$ at 4.2K. Magnetic field studies are in progress.

Along with multifilamentary Bi-2223 tapes, current leads of various sizes of Bi-2223 tube conductor and of Bi-2223 rod conductors which are needed for high current transport were also developed. Studies on more than fifty tubes (L=10 cm, O.D.=1.2 cm, I.D.=1.0 cm; L=20 cm, O.D.=3.0 cm, I.D.=2.8 cm; L=30.5 cm, O.D.=1.2 cm, I.D.=1.0 cm) and fifty rods (L=10 cm, D=0.5 cm and 0.7 cm) confirmed more than 60% reproducibility of $I_c > 150 \text{A}$ at 77K under self field (Fig. 4.9).

The fabrication of 30.5 cm long tube conductor needs a special mould, which has been developed by us. In the process of development of 30.5 cm long bulk tubes and rod conductors (perhaps, the first such indigenous development) the group has evolved a new initial sintering process, which appears to produce required $I_c$ values in a shorter interval of time.

Under the development of ceramic filters for automobile and other engine exhausts the fabrication process for the filter for 10 Bhp Engine was standardized (Figure 4.10).

Problem of filter breakage could not however be solved by only material design. It could be handled by innovative ways of packing the filter in the mechanical system. New compositions for porous ceramics were investigated. Uniaxial pressing of NaCl: Al$_2$O$_3$ was used to prepare new porous ceramics. Its processing parameters were investigated. It was found from crashing strength measurements and SEM method that porous bodies strength decrease with addition of NaCl (Figure 4.11). Optimum sintering temperature for Al$_2$O$_3$: NaCl was investigated by XRD Method. A project on microwave sintering of beta Alumina tubes was initiated.

![Fig. 4.9: Tube and rod conductors of Bi-2223 of various sizes: A/B tube conductors of 30 cm length, C/D/E/F rod conductors of Bi-2223 HTSC (not to scale)](image)

![Fig. 4.10: Bhp diesel engine filter](image)
Electrochromic Materials and Devices

Smart Electrochromic Windows for Energy Conservation

The main goal in this as well as the in-house project is ultimately to fabricate low cost prototype large area Electrochromic Windows (ECWs). This needs bulk preparation of the precursor materials for both the primary as well as counter electrodes. The last step of the sol-gel process developed earlier for preparing the precursor material for depositing WO$_3$ films involves drying of the solution at low pressure and for bulk preparation use of a diaphragm pump & a rotary evaporator ensures contamination-less uniformly dried precursor material.

Fabrication of a few ECWs of dimensions up to 4” x 4” and investigation of their performance characteristics were carried out earlier. However, the constraint of preparation of bulk precursor material didn’t allow us to scale up the window area. But then we focused our attention to an alternate technique that would give WO$_3$ films of comparable or better electrochromic performance preferably at a lower cost. The technique adopted was electrodeposition of WO$_3$ films using the solution in the sol-gel process, before drying, as mentioned above. With an appropriate dilution and eliminating the drying step the films could be easily electrodeposited. On the counter electrode part of the devices, development of two passive counter electrodes e.g. SnO$_2$: Mo and CeO$_2$: TiO$_2$ was undertaken. To overcome issues like short duration stability experienced in the former and need of high temperature around 500°C for both, developmental work on another potential active counter electrode Prussian blue was initiated, the films of which could also be deposited by Electrodeposition and needed no further heat treatment. Similarly for the third component of the ECWs namely the electrolyte, a new methodology was attempted which is likely to make the device packaging easier.

Thus all the work carried out during this year was directed towards easy preparation of the electrodes and the electrolyte that would result in ECWs with improved performance characteristics, possibly at a lower cost.

Electrodeposition of WO$_3$ Films

Peroxotungstic acid (PTA) or Acetylated PTA (APTA) as such and with chemical additive have been the precursor materials prepared and used to deposit WO$_3$ films. Extensive investigations have been carried out in the past in understanding the chemistry of the various steps involved, the properties of the WO$_3$ films prepared, roles of different additives, complexing agents etc. Best films prepared were characterized to have a small volume of nanocrystallites in an amorphous matrix resulting in faster kinetics.

The technique of electrodeposition was found to be advantageous. As mentioned above, it eliminated the step of drying under vacuum. With the available potentiostat we could easily deposit the films of WO$_3$ by cathodic reduction of PTA in alcoholic medium. The films were also prepared using APTA in alcoholic medium. Elaborate investigations have been carried out.
using the techniques XRD, SEM, TEM. The electrochromic characteristics have shown superior properties than the films made by spin coating the alcoholic solutions of PTA & APTA solid precursor materials. Our preliminary TEM studies have shown the films to be nanocrystalline. More detailed investigations of the films at different stages of heat treatment and their correlation with the properties are underway.

**Electrodeposited Prussian Blue Films as Active Counter Electrodes**

Prussian blue films have complimentary properties with respect to WO\(_3\) films i.e. these films in the oxidized state have blue colour similar to that shown by WO\(_3\) films in their reduced state and they become transparent respectively in their reduced and oxidized states. As a result, when used with an electrolyte separating them, the resultant electrochromic transmissive devices are expected to show superior optical transmission modulation.

This work has been just initiated. Electrodeposition of Prussian blue films by constant current is being attempted.

**Chemical Polymer Gel Electrolyte**

Starting from the liquid electrolytes and trying a variety of electrolytes over the years, the group has successfully made PMMA based gel polymeric electrolytes, incorporated them into prototype ECDs and established their suitability for window applications. However, their use necessitates good sealing / lamination of the devices. Instead of such a physical gel - wherein no chemical bond formation occurs between the liquid electrolyte and the polymer, a chemical gel has been attempted - wherein covalent bond formation occurs between the polymer chains - which comprises the conventional liquid electrolyte along with an acrylic monomer, a copolymer as a cross linker and another photo initiator. On irradiation with a UV lamp, photo polymerization takes place with the formation of the in-situ thick electrolyte film on one of the electrodes.

Such a polymeric gel electrolyte has been characterized by many techniques and its suitability for ECW applications has been checked.

Figure 4.12 illustrates the cyclic voltammograms of tungsten oxide, Prussian blue in one of the chemical gel electrolytes using Pt plate and Ag wire as counter and reference electrodes respectively. Figure 4.13 depicts cyclic voltammograms of an ECW (WO\(_3\) as primary and Prussian blue as counter electrodes) cell scanned between 0.6 V to -1.7 V (first and tenth cycle) in a two electrode system. Transmission characteristics (at \(\lambda = 650\) nm) of an ECW with a chemical gel (a) in coloured state (after precharging at -1 V for 60 seconds); (b) in bleached state by applying 0.6V for 30 seconds; (c) and (d) in coloured and bleached states respectively are again shown in figure 4.14.

All the three above mentioned attempts will definitely have a role to play for our future project work in which the commitment is to make large area ECWs.
Polymeric Materials and Devices

Poly(3-methyl thiophene) (P3MT) is one of the most promising materials from polyheterocyclics family having good environmental and chemical stability with excellent electronic and optical properties. We have synthesized poly(3-methyl thiophene) by chemical oxidation method in an inert atmosphere using ferric chloride as dopant. Samples of different dopant concentration have been synthesized and analyzed by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy, and direct current conductivity measurement. Synthesis of the polymer was confirmed by FTIR studies. FTIR spectra showed a shift in the heterocyclic bands in the region of 700-1200 cm⁻¹ with a decrease in temperature at which the synthesis of the polymer was performed. It was evident from the scanning electron micrographs that the surface structure of the polymer became denser with an increase in the doping level. The room temperature measured dc conductivity increased initially up to the doping level of 0.8 M and then this increase tended to slow down. Samples having a doping level of 0.4 M were synthesized at 300, 280 and 270 K while maintaining the other synthesis parameters. The conductivity and yield were found to increase as the temperature of the polymerization decreased. The dc conductivity of P3MT samples has been measured as a function of temperature in the low temperature region (77-300 K). The observed dc conductivity data were analyzed in the light of Mott’s variable range hopping (VRH) model. Different Mott’s parameters such as characteristic temperature (T₀), average hopping energy (W), average hopping distance (R), and the density of states at the Fermi level [N(E_F)] were evaluated. By taking the inverse of the coefficient of exponential decay of the localized states involved in the hopping process as 0.5 nm, a realistic value of density of states at the Fermi level [N(E_F)] has been obtained. The measurement of dc conductivity from 10-300 K on P3MT samples having different dopant concentration is in progress. Measurement of ac conductivity and dielectric constant in the temperature range 77-300 K and in the frequency region 100 Hz-10 MHz on the lightly doped samples of P3MT is also in progress.

The insulating emeraldine base (EB) form of polyaniline (PAN) and electrically conductive sulfuric acid and phosphoric acid doped emeraldine salts (ES) form of PAN were synthesized by chemical oxidative polymerization technique. Their vibrational spectra were studied in the region 4000-400 cm⁻¹ at ambient temperature by Fourier transform infrared (FTIR) spectroscopy. Infrared transmittance spectra of EB and ES were investigated to understand the bonding behaviour of different organic and inorganic groups present in the polymeric chains and their structural...
variations on protonation by sulfate or phosphate ion inclusion in the polymer salt network. These studies revealed the para-coupling of deformed disubstituted benzenoid (B) and quinoid (Q) rings with ends capped predominantly by B4Q1 units. The deformation of B and Q rings was confirmed by the appearance of many weak bands, very weak bands, and satellite structures in strong transmittance peaks of polymeric chain-constituting groups. Protonation takes place at the nitrogen sites of Q rings and forms semiquinone radical ions in ES. The vibrational bands pertaining to B rings, Q rings, B4Q1 units, semiquinone segment, sulfate ions, and phosphate ions were observed and assigned from these measurements. The shift in peak position of some bands with gain or loss in intensity and appearance of some new bands were observed in sulfuric acid and phosphoric acid doped ES spectra. These variations are attributed to the formation of new structural groups in ES on protonation and a change in crystalline field by sulfate and phosphate ion doping for cross-linking the polymeric chains through hydrogen bonding. The detailed analysis of dc conductivity and ac conductivity data of different doped forms of polyaniline (PAN) is in progress.

Samples of polypyrrole(PPY), poly(N-methyl pyrrole) [P(N M PY)] and their copolymer; poly(N-methyl pyrrole-pyrrole) [P(N M PY-PY)] were prepared by electrochemical polymerization technique. Their conductivity values were optimized for fabricating indium-polymer Schottky junctions. The current-voltage characteristics of the indium-polymer Schottky junctions were investigated. The results have been explained on the basis of thermionic emission theory. Out of the various polymers synthesized for the present investigations, the copolymer formed using monomers of 0.025 M pyrrole and 0.075 M N-methyl pyrrole having bulk conductivity ~ 10^-2 - 10^-3 Ω^-1 cm^-1 is a promising candidate, for making Schottky junction devices because of the better values of the ideality factor (η) ~ 1.48 and the rectification constant (ρ) ~ 1808. The current density and Chot plot as function of bias voltage are shown in Figs 4.15 and 4.16 for different conductivity values of copolymer, P(N M PY-PY). Search for other conducting polymers with suitable conductivity values for making Schottky junction devices is under investigation.

Synthesis of composites based on lead titanate (PbTiO₃) and barium titanate (BaTiO₃) dispersed in a piezoelectric polymer poly vinylidene fluoride (PVDF)
matrix have been undertaken. The composites were formed using sintered PbTiO$_3$ and BaTiO$_3$ powder dispersed in PVDF granules using dimethylformamide (DMF) as the solvent. Smooth films (thick ~ 1 mm) of PbTiO$_3$/PVDF and BaTiO$_3$/PVDF composites were developed. The dielectric and piezoelectric measurements were carried out on the poled films of the composites. The results indicate that the measured values of dielectric constant ($\varepsilon'$) and piezoelectric charge constant ($d_{33}$) were strongly influenced by the relative proportions of the two constituents and the poling conditions. The dielectric behaviour of these composites can be explained well by Yamada's relation, which furnishes a unique method to tailor these composites. The present study indicates that the effective field acting on the grain is a fraction of the actual applied field, which puts an upper limit on the $d_{33}$ coefficient using conventional poling methods. This points out the fact that alternative technique such as corona poling should be adopted for getting better characteristics of these composites.

The synthesis and characterization of polypyrrole/sodium nitrate (PPY/NaNO$_3$) composite films have been undertaken for its possible use as a substrate to support endothelial cell proliferation and the dc conductivity of the film has been measured as a function of temperature. The analysis of the observed dc conductivity data is in progress using different models of mechanism of charge transport.

The conducting polymer has a unique property of having large number of charge carriers in their polymer backbone. Keeping this in view the conducting polymer membranes have been developed for capturing viruses through electrostatic interactions of charges between viral particles and the polymer because RNA protein of virus contains some intrinsic charges. Various combinations of pyrrole and N-methyl pyrrole monomers were tried in order to get optimum value of conductivity and environmental stability of the membrane. Then these membranes were prepared at different temperatures in an inert atmosphere using the required amount of pyrrole and N-methyl pyrrole monomers. These prepared conducting polymer membranes have been tested for virus retention on it by Department of Microbiology, All India Institute of Medical Sciences (AIIMS), New Delhi. Results indicate that some of the membranes retain almost 100% viruses. A prototype of Water Purifier has been designed and fabricated using the above said membrane and other available materials and is being tested for its efficacy.