इंजीनियरी पदार्थ
ENGINEERING MATERIALS
इंजीनियरिंग पदार्थ योजना के अन्तर्गत धातु एवं मिश्रधातु, उन्नत कार्बन उत्पाद, महत्व और पालीमरिक पदार्थ व द्रव्य क्रिस्टल अनुभागों का समूह है। यह विभाग पदार्थों के संसाधन और घटकों, युक्तियों तथा यंत्रों इत्यादि के विकास में कार्यरत है। इस उच्च कोटि के निर्माण के और महत्वपूर्ण द्रव्यों का उपयोग कैनिस्टर पदार्थों, मिश्रण, उन्नत कार्बन उत्पादों, विद्युत-प्रकाशीय-इलेक्ट्रॉनिक युक्तियों के निर्माण में किया जाता है। इनमें द्रव्य-क्रिस्टल, स्वास्थ्य संबंधी और विशेष-गैसों की मानस्तता युक्तियां भी शामिल हैं।

विभिन्न अनुसंधान और परिक्षण संस्थानों व निजी तथा सार्वजनिक सेक्टरों द्वारा प्रयोजित, सहयोग और परामर्श परियोजनाओं का संचालन सफलतापूर्वक पूर्ण किया है। इस वर्ष सीएसआईआर नेटवर्क की चार नयी परियोजनाएं शुरू की गई हैं।
The Division of Engineering Materials mainly comprises of Metals & Alloys, Advanced Carbon Products, Soft & Polymeric Materials and Liquid Crystals Groups. The division has been actively engaged in the material, process and technology development for components, devices and systems, in a variety of areas. These materials, for high performance and strategic applications, include aerospace metallic materials, composites, advanced carbon products, and electro-optical and opto-electronic devices, including liquid crystals, health-care and toxic gas monitoring devices.

Several development projects, including sponsored, grant-in-aid, collaborative and consultancy projects have been successfully completed for different R & D organizations, both, in the public and private sectors. This year four new CSIR Network projects have also been initiated.
Metals & Alloys

Development of different grades of Magnesium and Aluminium light weight alloys and their components

The work was mainly concentrated in developing light weight Magnesium and Aluminium alloys and their components mainly to evaluate their application for aerospace and automobile applications. The synthesis of Mg-alloy, with rare earth alloying additions (Mg-Zn-Y-Zr and Mg-Y-Zn), using spray forming followed by secondary processing, was taken-up under an on-going VSSC sponsored project. Under the In-house project, work was carried out to synthesize magnesium structural alloys (Mg-Al-Zn) using spray forming and characterize the products. Other project on secondary processing of Mg-alloys using Equal Channel Angular Extrusion Process (ECAP), which is state-of-the-art metal forming technology, was initiated.

The synthesis of Al-alloys (Al-12Si) employing spray atomization and deposition technique was also undertaken in order to obtain refined and equiaxed microstructure resulting in improved properties.

Magnesium Alloys

The main attractive feature of Mg-alloys is its low density (1.72 gm/cc) as it is one of the lightest engineering alloys and thus possesses high specific strength leading to potential weight saving in aerospace and automobile industry. The opportunities offered by magnesium alloys in terms of high specific strength, improved chemical resistance, good hot-forming, machinability and weldability characteristics have opened new avenues for their usage in aerospace and automobile industry.

The main driving force for the development of Mg-alloys using spray forming is the quest for lighter materials with better microstructural features leading to improved mechanical properties, which have prompted the development of these alloys. Currently, Mg-alloys are synthesized using conventional liquid metallurgy technique, which have an inherent problem of defects in form of microporosity arising due to gas entrapment, dendritic microstructure associated with casting and surface oxidation due to its affinity for oxygen, all of which are detrimental for its mechanical properties. However, these alloys synthesized employing spray forming have fine and reduced grain size resulting in a refined and equiaxed microstructure with no indication of dendritic features normally observed with cast alloys. The inert conditions required for atomization and deposition minimizes surface oxidation and other deleterious surface reactions, especially for reactive materials like Mg-alloys. All these lead to enhancement of mechanical properties of Mg-alloys synthesized using spray-forming technique.

Vikram Sarabhai Space Centre (VSSC) sponsored project entitled, “Spray forming technology of Magnesium alloys”

The main objective of this sponsored project was the development of spray forming technology for different Mg-alloy systems by optimization of process parameters for each system and to secondary process these spray formed products using hot forging and to supply 20 blocks of spray formed /forged plates to VSSC after characterization.

Under this project, work was taken up to spray-form Mg-alloys with Yttrium as rare earth alloying element, which increases the temperature capability of these alloys. Experiments were conducted to spray-form two systems of these alloys, namely, Mg-Zn-Y-Zr and Mg-Y-Zn alloy on the existing spray atomization and deposition unit using about 5–7 kgs of melt. Various process parameters such as melt temperature, gas pressure, flight distance, delivery tube etc., are being optimized in order to obtain as-spray deposits with good density, yield and fine equiaxed microstructure. The spray-formed products were secondary processed using hot-forging on the 500-ton vertical hydraulic press.

Complete metallurgical, microstructural characterization and mechanical testing of these spray-formed products is also being carried out at NPL and simultaneously these are characterized at VSSC,
Thiruvananthapuram. It was observed that the elongation improved on spray forming followed by forging, but the tensile strength only improved marginally. Efforts are presently underway to improve the tensile strength by optimizing the primary and secondary processing parameters.

12 spray-formed blocks of Mg-alloys, with Yttrium as rare earth alloying element, in two different alloy systems, have already been supplied to VSSC for testing and evaluation. Work is currently underway for completing the process parameter optimization of spray forming for Mg-alloys with Yttrium as alloying additions based on the mechanical and metallurgical characterization results and to finally supply the remaining spray-formed blocks of Mg-alloy to VSSC, Thiruvananthapuram.

**Development of Light Metals/Alloys and their Component**

Under this in-house project, work was carried out to spray-form Mg-alloy (Mg-Al-Zn) using the existing spray atomization and deposition unit. Various process parameters were optimized in order to obtain dense product with low grain size. Typical yields of the spray formed Mg-alloy deposits were found to be in the range of 60-65% of the weight of the melt. Microstructural characterization using optical microscopy, scanning electron microscopy, X-ray diffraction, and mechanical characterization using universal testing machine has been carried out on the spray formed products. The as-sprayed deposits of these alloys had a fine-grained microstructure with a density of about 93-95% of the theoretical density.

These as-sprayed Mg-alloy deposits were secondary processed employing forging technique using the specially designed forging tooling on a 500-ton vertical hydraulic press. Various forging parameters were optimized so as to obtain a dense product without any cracks. The density of the sprayed Mg-alloy deposits after forging was found to increase to near the theoretical density. The mechanical properties of the hot-forged Mg-alloy were found to be slightly higher than those of the equivalent ingot product. However, the hot-forged alloy exhibited high elongation values (~10%) over those of the equivalent ingot product (~7-8%) which could be attributed to microstructural refinements achieved by spray forming and forging processing.

The optical microscopy of the cast Mg-alloy starting material indicated a non-uniform microstructure with average grain size of about 200–300 µm. Fig. 3.1 shows the microstructure of the spray-deposited and forged Mg-Al-Zn alloy. This figure clearly shows equiaxed microstructure consisting of 40–90 µm cells of magnesium. Efforts are underway to further optimize the process parameters in order to obtain fine-grained microstructure throughout the as-sprayed deposit and to improve the mechanical properties of the spray-formed and forged products.

**Secondary processing of Magnesium Alloys using Equal Channel Angular Extrusion**

Equal Channel Angular Extrusion Process (ECAP) is an important state-of-the-art metal forming technique that is capable of producing uniform severe plastic deformation in a variety of materials, without causing significant change in geometric shape or cross section. ECAP realizes the method of ‘Simple Shear’ which can be considered as a ‘near ideal’ deformation method for
structure and texture formation in metal-working. One of the main advantages of this technique is the uniform and unidirectional deformation that can be produced under relatively low pressure for massive products. Multiple passes in ECAP leads to high plastic strain in the bulk material, thereby refining the microstructure. More importantly, by changing the orientation of the billet between successive passes, complex microstructures and textures can be developed.

Developmental work has been initiated to produce ultra-fine grained microstructures in bulk Mg-alloys using Severe Plastic Deformation (SPD) technique. Experiments are underway employing Equal Channel Angular Extrusion to obtain finely-grained microstructures in Magnesium alloys (Mg-Zn & Mg-Al) in order to improve their mechanical properties. The total set-up consisting of the die assembly for ECAP experiments was designed and got fabricated for an included angle of 120° and a few trial runs for the processing of Mg-alloys using this technique were conducted. Initial trial experiments using the 120° angled die were carried out on Mg-alloys. Work is presently underway to modify the die design and fabricate fresh sets of die assemblies with 105° and 90° die-angles for further experiments. Furthermore, the hydraulics of the existing set-up is also being modified by incorporating hydraulic back pressure to the existing system for more effective performance.

**Extrusion Technology for Magnesium Alloys**

A MoU was signed by Dr. Vikram Kumar, Director, NPL and Dr. Alan Taub, Executive Director, General Motors (USA) for a project on the Development of Extrusion Technology for Magnesium alloys, to be undertaken by NPL. The main objective of this project is to optimise extrusion process parameters (die design, temperature, strain rate and extrusion ratio) and to carry out detailed characterization to obtain high quality extrusions with improved strength and ductility. This project although has been sanctioned, in principle, but a final approval from General Motors, USA, is still awaited.

**Aluminium alloys**

The synthesis of Al-alloys (Al-12Si) employing spray atomization and deposition technique was undertaken in order to refine the microstructure resulting in improved mechanical properties. Some preliminary work was also done to synthesize Al-Si alloys/SiCp metal matrix composites, using stir-casting technique.

**Spray forming of Al-Si alloys (Si~12%)**

Al-Si is an important material due to its properties, like high wear resistance, low CTE, high thermal conductivity and good strength. These properties make it suitable for automobile piston application.

Under an in-house project, a few preliminary experiments were conducted to spray deposit Al-Si alloys (Si ~12%) on the spray forming unit. The mother alloy used for spray forming exhibited a typical dendritic microstructure with needle-shaped Si embedded in a Al-alloy matrix, as shown in Fig. 3.2. However, on spray

![Fig. 3.2 : Microstructure of cast Al-Si alloys (X 200)](image)
forming the cast dendritic structure of the mother alloy was broken down and a finely grained necklace-type microstructure was obtained, with finely shaped micron sized Si particles nucleating on the grain boundaries of the Al-matrix, as is clearly evidenced from Fig. 3.3. This work will be continued to spray deposit hypereutectic compositions of Al-Si alloys (Si > 12 wt%) employing rapid solidification processing.

Development of Oval Shaped Tube as Skid Landing Gear for Advanced Light Helicopter

This project was sponsored by Hindustan Aeronautics Limited, Bangalore, and was sanctioned in two phases and formed the technology development package for the development of oval shaped tube as skid landing gear for Advanced Light Helicopter. After successfully demonstrating the technology developed for the Oval Shaped Tube as Skid Landing Gear for Advanced Light Helicopter, an official communication has been received from Hindustan Aeronautics Limited, Bangalore, mentioning that the development of oval skid tube followed by subsequent annealing and heat-treatment of skids have been successfully completed.

Advanced Carbon Products

Development of Carbon-Ceramic Composites

C-SiC-B₄C composites refer to a special class of carbon based materials which cover the main drawbacks of carbon, particularly its proneness to air oxidation, while essentially retaining its good properties. Several series of experiments were conducted to develop C-SiC-B₄C composites exhibiting high oxidation resistance at temperatures in the range of 800-1200°C. The aim of the experiments was to study the effects of carbon-to-ceramic and ceramic-to-ceramic ratios on the oxidation behaviour and other characteristics of the C-SiC-B₄C composites. Good compositions of composites made in the form of small rectangular plates using unidirectional moulding have been found out, which have shown almost zero weight loss (<0.5%), or even weight gain, referring to high oxidation resistance at temperatures of 800-1200°C.

Synthesis of Al-Si/SiCp Metal Matrix composites using stir-casting technique

Efforts were continued in an in-house project for the development of Metal Matrix Composites using stir-casting vortex technique employing mechanical stirring. Preliminary experiments were carried out to synthesize metal matrix composites with Al-12Si as the matrix material and 5 wt% of SiCp as the reinforcement. The results indicated a non-uniform dispersion of the reinforcement in the Al-Si matrix with a lot of agglomeration of reinforcement particulates in the matrix. Work is underway to improve the dispersion of SiCp in Al-Si to improve the distribution of reinforcement in the Al-Si matrix.
for a residence time of 3–10h. Significant improvement in the strength of C-SiC-B₄C composites has been observed which increases with an increase in the total ceramic content and the SiC : B₄C ratio. Further work including isostatic moulding of the C-SiC-B₄C composites is in progress.

**Carbon Nanotubes**

Carbon nanotubes were synthesized using different systems. Various parameters, e.g., He gas pressure, voltage, current etc., were optimized and good reproducibility was established to produce carbon soot containing nanotubes. Detailed characterization through SEM, TEM, TGA and XRD revealed that the soot contained at least 50% of carbon nanotubes. Systematic studies are in progress to isolate the pure nanotubes from these carbon deposits.

**Synthesis of Silicon Carbide Nanofibres**

Silicon Carbide (SiC) nanomaterials possess excellent oxidation resistance apart from improved mechanical properties and are suitable candidates for the development of metal matrix and ceramic matrix composites with superior mechanical and thermal properties. Preliminary investigations were carried out to synthesize SiC nanofibres by combining polymer blend and sol-gel techniques. Silicon alkoxides were hydrolysed along with the thermoplastic polymer having a carbon residue on pyrolysis and the resulting polymer incorporated with sol-gel silica was heat treated to 1400°C to get a mixture of SiC nanofibers, carbon and traces of silica. Carbon in the mixture was removed by oxidation at 700°C and the formation of SiC nanofibres was confirmed through SEM and TEM studies. Further work is in progress to synthesize SiC nf using different alkoxides and polymers.

**High Thermal Conductivity Carbon-Carbon Composites**

PAN based T-300 carbon fibres were used to develop carbon-carbon composites of size 150 mm x 50 mm x 5mm. The main objective of these studies was to improve the density of the carbonized composites after first carbonization cycle (HTT = 1000°C) to at least 1.5 g cm⁻³. Experiments were performed with different fibre volume %, namely, 50%, 55%, 60% and 65%. A modified pitch with a softening point of 214°C and coking yield of 76% was developed and used for the fabrication of green composites. It was observed that by increasing the fibre volume content to 60%, the density of the carbon-carbon composites after two impregnation cycles got increased to a value of 1.47 g cm⁻³ which is a significant achievement. Further experiments are in progress in this direction.

**Development of Low-PAH Coal Tar Pitch**

Work was initiated on development of coal tar pitches with a reduced content of polycyclic aromatic hydrocarbons (PAHs), under a project sponsored by the Ministry of Environment & Forests, New Delhi. Two methods, both involving the physical removal of B(a)P, namely, (1) distillation under partial vacuum and (2) solvent extraction of coal tar pitches, were employed. It was observed that both the methods are able to reduce the B(a)P content in both the varieties of coal tar pitches – a binder-grade pitch and an impregnating-grade pitch. However, the solvent extraction method appears to be better of the two because, for similar yield of the resultant pitch, it causes a considerably higher decrease in the B(a)P content along with a much lower increase in the other characteristics of the resultant pitches. Further work including the use of inexpensive/industrial solvents for the purpose of solvent extraction is in progress.

**Consultancy Project**

The on-going consultancy project, sponsored by M/s. Graphite India Limited, Bangalore, on the ‘Upscaling of green coke based high density graphite technology’ was continued. The company’s engineers were advised to develop the intermediate coal tar pitch and imparted training to develop the green coke on a 3 kg batch size. The green coke was ground into a fine powder and...
characterised. The isostatic moulding of the green coke powder into blocks and their subsequent carbonisation to 1000 °C, followed by graphitisation to 2600 °C, are in progress.

**Polymeric & Soft Materials**

**Conducting Polymers**

**Synthesis of Conducting Polymers**

There are numerous conducting polymers that have been developed so far, but polyanilines, poly (3,4-ethylenedioxythiophene) and substituted poly (phenylene-vinylene) have been the subject of intensive research because of their technological applications in a variety of devices, such as, electrostatic charge dissipation (ESD), electromagnetic interference (EMI) shielding, organic light emitting diodes (OLED), opto-electronic devices, corrosion prevention, super capacitors and sensors.

Polyaniline stands for its ability to form processable conductive form which is environmentally stable. However, the presence of benzidine moieties in the polymer backbone, which might yield toxic products, have hampered its technological utility in numerous industrial groups. We, at NPL, have synthesized polyaniline which is processable and free from benzidine and thus can be used for many industrial devices. GC-mass spectra of the polyaniline, synthesized in conventional inorganic acid medium (Fig. 3.4) and that synthesized in specific organic dopant system, shows the absence of benzidine (Fig. 3.5). Fig. 3.4 : GC-Mass Spectra of filtrate obtained during synthesis of polyaniline using inorganic protonic acid

Polymerization of aniline in the presence of mixed dopants has yielded a polymer which is processable and soluble. It has been observed that the resultant conducting polymer possesses better thermal stability and processability compared to when the synthesis had been carried out in the presence of conventional aromatic dopant system. Blending of conducting polymers doped with mixed dopants was carried out with conventional insulating polymers like low-density polyethylene (LDPE), acrylonitrile-butadiene-styrene (ABS), polystyrene (PS) etc. Blends so obtained have been tested for their utilization as antistatic composite materials.

Fig. 3.5 : GC-Mass Spectra of filtrate obtained during synthesis of polyaniline using organic protonic sulphonie acid

Synthesis of conducting polymer polyaniline in the presence of ferrofluids and ferro-organic dopants have yielded quite interesting polymers and the resultant polymers are under investigations and their characterization is being carried out. Flexible conducting polymer ferro-fluid composites have been
designed which can find applications in EMI shielding, ESD, microwave absorption and radar absorbing materials (RAM).

Conjugated polymers based on benzene have been of interest for their applications in organic light emitting diode devices. These polymers may challenge the conventional materials used in the fabrication of OLED devices. NPL has synthesized some of these conjugated polymers and the devices are being tested in OLED lab for electroluminescence studies.

**Organic Light Emitting Diode**

There is a growing interest all over the world in the electroluminescence of organic materials. This is due to the prospect of it being used in high density flat panel displays. NPL is working in the field of organic electroluminescence for the last four years. We have the facility to synthesize small molecules and conjugated polymers as well as the facility to fabricate organic LEDs using these materials.

Among these electroluminescent conjugated polymers, poly(2-methoxy), 5-(2’-ethyl-hexyloxy-p-phenylene vinylene) (MEH-PPV) is a very important polymeric material which has got high luminescence properties as well as the required electrical and mechanical properties for polymer LED applications. NPL has succeeded in synthesizing this key material. The photoluminescence spectra of NPL synthesized MEH-PPV is given in Fig. 3.6.

The electrical and photoluminescence characterization of MEH-PPV are in progress. Blue electroluminescent materials are very important for the development of full colour organic light emitting diodes. The laboratory is also working on the synthesis, characterization, and fabrication of devices based on small molecules. One of the important material in this regard is the blue emitting aluminum complex material AlqM₂OH. This material has been prepared by the reaction of methyl substituted hydroxy quinoline with aluminum hydroxide. The new material has been characterized using optical and infrared spectroscopy, thermo-gravimetric analysis and luminescence spectroscopy.

A comparative study of luminous efficiency of our new materials with Alq₃ obtained from Aldrich (Fig. 3.7) was done. The PL efficiency of Almq₂OH and Mg (mq) were compared with Alq₃ obtained from Aldrich (99.5%).

Our result shows that the PL efficiency of Almq₂OH (OH) is about four times more fluorescent than commercially available Alq₃. The device fabrication and performance analysis of organic light emitting diodes is in progress at NPL.

![Fig. 3.6: Photoluminescence of MEH-PPV](image)

![Fig. 3.7: Solid state fluorescence spectra; excitation 400nm](image)
Development of Polymeric Sensors

Prepared doped and undoped polyaniline thin film sensors for detection of geotrichum (bacteria responsible for milk spoilage) and microbacterium Tuberculosis (TB). We have studied at NPL the optical, electrical and structural characterization of the vacuum deposited polyaniline thin films by SEM, X-ray and electron diffraction techniques. These thin film polymer based microbial detectors are inexpensive, and are operated at room temperature, and thus have the advantage of remote positioning and monitoring at hazardous places. We have also studied the preparation of behavioural acceptance test on the above mentioned sensors for sensitivity, selectivity, specificity, response time, decay and recovery towards geotrichum and microbacterium tuberculosis. Initiated the necessary electronics for development of audio/visual alarm. Basic studies on vacuum deposited polyaniline thin films like measurement of thermal properties form room temperature to 170°C and band gap determination from reflectance measurement have been carried out.

Biomolecular Electronics

Polyaniline Based Micro-actuator

An experimental set-up has been designed and fabricated to study the electrochemical properties of a thick film of conducting polymer under load (Fig. 3.8). Extension of the films versus voltage has been measured in terms of change in capacitance of parallel plate capacitor constituted by metals pan and a fixed metal plate. HP 4284A impedance analyzer measures absolute value of the capacitance. Change in capacitance is related to change in distance by pre-calibrating the assembly using travelling microscope. A computer programme is developed to convert the capacitance value with the corresponding distance and simultaneously plotting the graph between changes in length of polymer film versus applied voltage (Fig. 3.9). The assembly has been used to study the electrochemomechanical behaviour of solution cast polyaniline films (~50µm thick). During first cycle the length is enhanced by about 6% of the original value, while repetitive value of extension is ~2.8% in subsequent cycles.

Cholesterol Biosensor

Cholesterol esterase (ChEt) and cholesterol oxidase (ChOx) enzymes have been physically adsorbed on electrochemically prepared Poly (An-FAn) polymeric films (Fig. 3.10). ITO glass plates have been used as substrate for film deposition. The attempts were made to characterize these Poly (An-FAn) based enzyme films with respect to the effect of cholesterol palmitate and cholesterol concentration, applied potential, pH, temperature and storage time, using spectrophotometric and amperometric techniques.
**DNA Biosensor**

Polypyrrole films have been synthesized electrochemically on platinum disc electrode and DNA was physically adsorbed on it. After the immobilization of DNA on polymeric films, it was used to study the effect of various toxicants such as o-chlorophenol on oxidation current. DNA has conducting property due to movement of electrons through oxidation of guanine base. When o-chlorophenol forms an associated molecule with DNA it obstructs the flow of electrons. This causes reduction in oxidation of guanine and reduced current is observed. The effect of o-chlorophenol on the oxidation peak is shown in Fig. 3.11.

**Glucose Biosensor**

**Glucose biosensor based on poly-3-hexyl thiophene**

Glucose biosensor based on poly-3-hexyl thiophene Langmuir-Blodgett films has been fabricated. These Langmuir-Blodgett films have been prepared by simultaneous entrapment of glucose oxidase and transferred onto the indium-tin-oxide coated glass plates. The P3HT/SA/GOX electrodes have been characterized by FTIR spectroscopy and response studies have been performed with respect to glucose concentration, temperature and storage time. The linearity was achieved in the range of 100 to 500 mg/dl with shelf life of about 75 days. Fig. 3.12 shows the response current of a P3HT/SA/GOX electrode as a function of temperature in presence of 100 mg/dl glucose concentration.

**Glucose biosensor based on the poly(2-fluoroaniline)**

Poly(2-fluoroaniline) has been electrochemically deposited on the ITO coated glass plates in the forms of thin films using 4M perchloride acid as electrolyte. Glucose oxidase (GOX) has been immobilized on to these electrochemically deposited conducting poly(2-fluoroaniline) films by physical adsorption method. The redox characterization of Poly(2-fluoroaniline) and Poly(2-fluoroaniline)/GOX films has been carried out by cyclic voltametry techniques. The electrode carrying

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**Fig. 3.10**: Photometric response of poly(An-FAn)/ChEt/ChOx enzyme films as a function of cholesterol oleate concentration (mM)

**Fig. 3.11**: Effect of 100 ppm O-Chlorophenol on oxidation of DNA

**Fig. 3.12**: Response current of a P3HT/SA/GOX electrode as a function of temperature in presence of 100 mg/dl glucose concentration.
GOX was found to be stable up to 32 days. The amperometric response of the Poly (2-fluoroaniline)/GOX electrodes at different glucose concentration (1.0-33 mM) and found to be linear from 1.0 to 18 mM (Fig. 3.13). The response time of these Poly (2-fluoroaniline)/GOX electrodes was found to be about 70 s.

**Lactate biosensor**

Lactate biosensor has been developed based on electrochemically entrapped polyaniline into sol-gel derived tetraethyl orthosilicate (TEOS) films coated on ITO glass plates. The ITO/sol-gel/PANI electrodes were utilized to fabricate a lactate biosensor based on actate dehydrogenase. A sol-gel/PANI composite obtained through electro-entrapment was found to provide environmental stability to the biosensor. Increased stability and linearity as the biosensor were also observed before and after polyvinyl chloride (PVC) coating. The amperometric response of the electrodes under optimum conditions exhibited a linear relationship from 1 mM to 4 mM. These sol-gel/PANI/LDH electrodes have a response time of about 60 s, a shelf life of about 8 weeks at 0-4°C. The linearity of the sol-gel/PANI/LDH electrodes obtained by coating an external layer of PVC on to these electrodes has been found to be up to 10 mM for lactate with a correlation coefficient of 0.89. The effect of the pH on the response of sol-gel/PANI/LDH films with and without a PVC coating is shown in Fig. 3.14. Table 3.1 represents the effect of interferents i.e. glucose, uric acid, ascorbic acid and glutamic acid etc. The response of sol-gel/PANI/LDH films with and without PVC coated in the presence of glucose (100 mg/dl), ascorbic acid (25 mg/dl), uric acid (35 mg/dl) and glutamic acid (25 mg/dl) were observed. Results were obtained that the effect of interferents was much more in the sol-gel/PANI/LDH films compared to films coated with PVC.

<table>
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<tr>
<th>Interferent</th>
<th>Response without PVC coating A</th>
<th>Response with PVC coating A</th>
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<tr>
<td></td>
<td>Before addition</td>
<td>After addition</td>
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<tr>
<td>Glucose (100 mg/dl)</td>
<td>15.6</td>
<td>16.8</td>
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<tr>
<td>Uric acid (35 mg/dl)</td>
<td>15.6</td>
<td>16.4</td>
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<tr>
<td>Glutamic acid (25 mg/dl)</td>
<td>15.6</td>
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<td>Ascorbic acid (25 mg/dl)</td>
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**Liquid Crystals**

Liquid crystals constitute a fascinating phase of condensed matter in between isotropic liquid and anisotropic solid.
There are several types of liquid crystalline phases like nematic, smectic, discotic etc. In smectic structure the molecules are packed in layers, side by side within the layer but end to end from one layer to another. The chiral tilted smectic phases show the ferroelectric behaviour. In ferroelectric liquid crystal molecules, where the layers are arranged in the form of helix and can be suppressed either by surface effect or by applying an electric filed. It (helix suppression) can be achieved by making thickness of the cell less than the pitch value so that surface effect is strong enough to unfold the helix. Such a phenomena is known as surface stabilized ferroelectric liquid crystals (SSFLC) and shows bistable or memory effects.

Another kind of chiral smectic phases, where pitch value is very short i.e. less than 1µm, are called deformed helix ferroelectric liquid crystal material. It uses a short-pitch mixture, where the smectic planes are oriented perpendicular to the bounding glass substrates. It is a linear effect and has no inherent bistability and as consequence, DHFLC exhibit no inherent optical threshold voltage. Another greatest advantage over the other FLCs is that the grey scale can easily be obtained using DHFLC material. It has been predicted and demonstrated at NPL that bistability is also possible in DHFLC at certain critical voltage and frequency region.

Bistability or Memory effect in surface stabilized ferroelectric liquid crystals (SSFLC) has been studied well but very few studies have been reported in the literature in case of Deformed helix ferroelectric liquid crystal (DHFLC). Recently at NPL, it has been tried to find out the critical conditions for bistability in DHFLC material. Bistability in DHFLC is based on electro-mechanical effect of helix deformation due to electric field. Bistability in DHFLC can be thought in a similar way, like the difference between ferromagnetic material and permanent magnet. It is a well established fact that when a ferromagnetic material is placed in uniform magnetic field, then small domains coalesce to form single domain. The spin-spin interactions come into play when the magnetic field is switched off and the sample becomes permanent magnet. On the same analogy, it might be possible that bistability in DHFLC exists due to helix unwinding under the application of electric field in which the dipolar interactions play a dominant role. As supported by the experimental results, elastic deformation may not be the only reason behind the memory since the memory is not transient. As experimentally observed, the memory effect is long lasting which implies that the elastic deformation energy is getting balanced by the dipolar interactions.

Fig. 3.15 shows the optical response of DHFLC at 20 volts and 10 Hz frequency. As one can see from the figure, optical transmission changes from maximum to minimum or vice-versa as applied field pulse reverses its polarity and there is almost no change when the applied pulse attains its 0 volt state. At higher frequency of 500 Hz (Fig. 3.16), there is degradation in the optical transmission at 0 V state, suggesting that at higher frequencies the memory state is not favoured. The memory effect in DHFLC material is also dependent on the applied voltage as shown in Fig. 3.17, even if the applied frequency is low (100 Hz). Therefore, the memory effect in deformed helix ferroelectric liquid crystal material depends on applied voltage and frequency unlike in other types of memory devices based on liquid crystal materials. The detailed dynamic study of such memory devices of DHFLC material is being carried out by electro-optical and dielectric spectroscopic methods.

![Fig. 3.15: Optical response of deformed helix ferroelectric liquid crystal (DHFLC) at 25°C in 3µm cell at 20V and 10Hz](image-url)
The essential optical coating in sun reflecting glass is palladium, silver or gold doped titanium dioxide film on glass substrates. The titanium dioxide film with high refractive index controls the reflectance where as the addition of Pd/Ag/Au dopands controls the absorption of solar sun spectrum. In this manner, buildings appear outwardly uniformly reflective.

Aesthetic appearance: White light transmission is controlled in accordance with sun exposure to minimize the cooling costs.

Presently, the titanium dioxide films can be prepared by physical vapour deposition technique, such as, vacuum evaporation and sputtering technique, chemical vapour deposition at normal and reduced pressure, sol-gel process by dip coating and spraying processes. In the vacuum coating technique, the substrate is held in a vacuum chamber and titanium dioxide is evaporated and then allowed to deposit on the surface of the substrate. The deposition can be carried out in vacuum unit in different ways, e.g., thermal evaporation, cathode sputtering, DC sputtering, RF sputtering and magnetron sputtering etc.

Dip coating process competes with vacuum coating method, spraying process and chemical vapour deposition process. The dip coating method has been explored and tested for technical feasibility and cost viability and has many advantages over the vacuum coating technique. The advantages of sol-gel process are:

(i) High degree of film thickness uniformity.
(ii) Simple thickness control
(iii) Better controlled stoichiometry
(iv) Low processing temperature
(v) Bigger sizes of substrates can be coated uniformly
(vi) Multi-layer deposition with widely varying optical characteristics
(vii) Applied to odd shaped substrates like tubes, pipes and rods.

Liquid Crystals and Self-Assembled Monolayer

Development of soft lithographic techniques for micro and nano-fabrication

Creation of small structures with feature sizes ranging from a few microns to sub-micron is of great technical relevance to materials science & engineering and biological sciences. Conventional photo-lithography is used routinely to fabricate
structures down to ~0.50 micron features in VLSI. The facility is prohibitively expensive and poses severe limitations for smaller feature sizes. Moreover, it has very little control over the surface properties of the structures that are very vital for chemical and biological applications. Soft lithographic technique utilizing micro-contact printing (µCP) of self-assembled monolayers (SAMs) has great potential in micro and nano-fabrication and would greatly compliment conventional photolithography.

Micro-patterning using micro contact printing, one of the variants of soft lithography, has been exploited to fabricate small structures on solid surfaces for microfabrication, sensors-arrays, MEMS and biological applications. It is an alternate (non-photolithographic) technique to create patterns in metal thin films on a substrate with feature sizes in sub-micron to micron range. It comprises of soft contact printing of SAM precursor solution using an elastomer stamp that contains the relief structures. The SAM solution is transferred to the well-defined regions on substrates having micron and sub-micron sizes. The surfaces derivatized with SAM serves as nano-thick etch resist and the uncoated surfaces could be etched in standard metal etchants. Micro-contact printing can be used repeatedly without invoking the costly equipment required in photolithography and is experimentally convenient and cost-effective. We, at NPL, are amongst the first ones to have initiated work on soft lithography and micro-contact printing in our country. We describe below the salient features of our work on soft lithography that would have direct relevance in device fabrication and biological applications.

Self-assembled monolayer of hexadecanethiol (HDT) is selectively transferred to the specific regions of the substrate with an elastomer stamp that is prepared by casting the liquid prepolymer of the elastomer against a master mask that has patterned relief structure on its surface. The elastomeric stamp was molded from a master (e.g., silicon chip) wherein structures with very small features were created by conventional photolithographic techniques. We have used poly dimethyl siloxane (PDMS) as the stamp material. The cured polymer could be easily peeled off from the master. The relief structure on the stamp is a replica of the pattern structure on the master and the depressions in the masters are the raised structures in the polymer stamp. The quality of the relief structure on the stamp has been found to have very high fidelity. The stamp was ‘inked’ with HDT solution and ink was transferred to the surface of the gold/silver films (500–5000 Å thick) films, deposited by thermal evaporation on glass or silicon substrates, by physical contact. The reaction of HDT molecules with gold/silver led to the formation of organized structure in the regions of contact leading to ‘autophobicity’ and exhibits contrasting physical and chemical properties. The ‘inked’ regions of the substrate act as good nano-resist film and the non-inked regions on the metal films could be easily etched by aqueous Na2S2O3, K3[Fe(CN 6)] and K4[Fe(CN 6)] solution.

Fig. 3.18 (Pl. see at next page) shows a SEM picture of an elastomer stamp cast from a silicon master. Fig. 3.19 shows a SEM picture of a pattern with feature sizes ranging from a few microns (<3µm) to several hundred microns (>100 µm) over large area (a few cm2) created on gold coated silicon substrate. Fig.3.20 (a & b) show the patterns of <3µm created in silver film on glass with sharp edge definition.
Fig. 3.18: SEM pictures of a PDMS stamp used for micro contact printing.

Fig. 3.19: Etched patterns in Au films on Si substrate with feature sizes ~15–60 micron using the PDMS stamp shown in Fig. 3.18.

Fig. 3.20: (a & b) Etched patterns in silver films on glass substrates with feature size <3 micron using microcontact printing.