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# Electret sensors, filters and MEMS devices: New challenges in materials research

Malti Goel

Recent advances in electret technology offer promise to serve mankind through medical prosthesis and by performing other biological functions. Increasingly, we recognize the challenge it has thrown to materials science research. How electrets are being put to use in sensors, actuators, filters and what micro-electro-mechanical system devices are emerging on the scene, are described here. This article also presents some of the highlights of early researches conducted in the field of electrets and current trends.

THE term electret was conceived as a counterpart of magnet about one hundred years ago. A dielectric material, which has been electrized (polarized) is called an *electret*. Thermoelectret effect was discovered in 1925, when Eguchi solidified a mixture of carnuaba wax, resin and beeswax in the presence of a high DC electric field<sup>1</sup>. The energy absorbed during the charging process resulted in space-charge polarization by trapping of positive and negative charges at the interstitial sites. Nadzakov<sup>2</sup> observed the photoelectret effect in 1937, by exposing a photoconducting dielectric to light radiation and electric field simultaneously.

Both thermoelectrets and photoelectrets are proving extremely important in modern sensing as well as optoelectronic devices. Their utility arises from the fact that they exhibit persistent polarization and a surface charge, which remain stable for a long time. A major breakthrough in electret applications occurred in 1966, when Sessler at Bell Laboratories introduced an electret con-

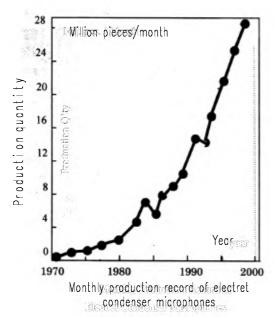
denser microphone (ECM). At present, ECMs are commercially being produced in large quantities<sup>3</sup> for use in tape recorders, stereos, telephones, cordless and cellular phones and hearing aids (Figure 1). The author<sup>4</sup> and her colleagues<sup>5</sup> also presented specific reviews on electrets in the early 1970s. In the recent years, excellent reviews and books on electret techniques and applications have been published<sup>6-9</sup>. This is an article on the importance and emerging potential applications of electrets and not an in-depth review.

In this article, starting from basic concepts of electret formation in dielectric materials and methods of study of polarization in them, applications in transducers and air filters as low energy-consuming, cost-effective pollution monitoring and control devices, having capability to filter toxic gases as well as suspended particles are discussed. With the advancement in materials research, miniature electret microphones integrated on silicon chips as microelectro-mechanical systems (MEMS) have been produced. Products employing electrets have been put into practical use in almost all walks of life. Use of electrets has been suggested for biomedical applications such as replacement of heart valve, bone implants and artificial muscles in robotic paradigm. Such developments have thrown new challenges in materials science research.

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The views expressed in this article are those of the author and not necessarily those of the organization.

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**Figure 1.** Growth in monthly production of electret condenser microphones from 1970 onwards (ref. 3).

## How to polarize a dielectric

An electret-forming material can be in the form of a sheet, a ribbon or a film coated on the electrode or any other form, which can maintain continuity and has two flat surfaces. As permanently charged material, an electret is formed by polarization in the presence of high electric field or by the application of corona or electron beam injection, in combination with heat or light. Three basic processes that can take place when a dielectric material is subjected to electric field are: (i) space charge polarization near the electrodes, (ii) bulk charges trapped inside the material at the interfaces or due to migration, and (iii) dipolar polarization due to polar molecules. Schematic of an electret showing different charge-trapping possibilities is shown in Figure 2.

In order to investigate dielectric properties of the materials, different poling methods are selected. 'Thermal poling' is the oldest method, in which a sample is heated under an applied electric field for a given duration and then cooled to room temperature, while still being energized. This method of electret polarization has been extensively adopted for polymers and other dielectrics, which have low melting point. The charge transport in such dielectrics is strongly dependent on temperature. In materials where charge dynamics is sensitive to light, 'optical poling' is adopted. It is similar to thermal poling, except that light is used in place of heat. It is found that the amount of stored electric charge in dielectric materials increases with poling time and poling field, till it saturates.

The two other charging methods, viz. corona charging and electron-beam injection are being applied to materials

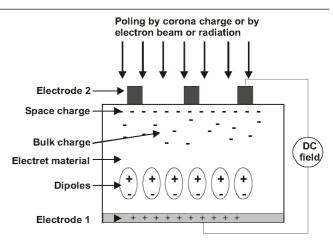


Figure 2. Different mechanisms of charge trapping in an electret material.

with higher melting point. In corona charging, a corona grid is placed over the material and the current flowing through the sample is maintained at a constant value. Surface potential can be measured simultaneously and it gives a measure of conduction phenomenon in the dielectric as well. In electron-beam charging, an electron gun is used. The sample is biased under the electric field and interstitial polarization is detected. A number of variations in these poling methods have been developed to suit the material and application in view.

## Measurement of polarization

A key parameter in understanding the charge storage and transport in dielectrics is the information about charge distribution and its decay with temperature or time. Measurement of space charge polarization in electrets gives important insights about the physics of dielectric materials. Polarization can be measured or scanned by relaxing the frozen charge using light, thermal and pressure-induced probes. Different techniques adopted for measurement of electret polarization are discussed below.

# Surface charge measurements

The charge on the surface of an electret can be directly measured by using an electrometer, which measures local, induced electric field. Such measurements are repeated at certain time intervals depending on the life of an electret. Between measurements, it is necessary to keep the samples in a short condition by wrapping it in an aluminum foil. This method was introduced in 1930s and is still being used for testing electret charge in dosimeters. To get information about volume polarization in an electret, sectioning technique has been proposed. Here, the polarized material is cut into sections and for each surface, charge is measured. This method, however, did

not gain popularity as it is difficult to slice an electret without disturbing its charge dynamics.

## Thermally stimulated discharge current (TSDC)

The discharge current of a dielectric is extremely weak at room temperature, but can be enhanced by light or thermal activation or by other means. The TSDC is the external current of the polarized sample, subjected to heating at a uniform rate. It has proved to be an extremely useful experimental technique to study dipolar behaviour or charge-trapping characteristics as well as to provide information on total internal charge stored. This technique has been perfected for the study of electret effect in polymers and biomaterials, as it provides information on different phase transitions as well as the total charge stored. The short circuit current *Js* is given by

$$Js = Ae^{KT}, (1)$$

where E is activation energy of the trapped charge, K is Boltzmann constant, T is temperature and A is a constant.

A graph of log Js vs T shows a discontinuity at certain temperature, which is the phase transition temperature of the material. From this, important material properties such as activation energy of the trapped carriers, their mobility and their lifetime in conduction state can be measured. Its only drawback is that it is a destructive method and the sample gets discharged in the process.

#### Photo-depolarization current

In photo-poled samples, direct irradiation with light gives rise to photo-depolarization current in the external circuit. It helps to understand the way in which charge is stored and is reactivated by optical radiation. Negatively charged and positively charged photo-poled samples show different decay rates due to different penetration depths of the trapped charge inside the material. This technique known for more than fifty years, has been recently applied for investigating corona-charged electrets made of silicon dioxide using monochromatic ultraviolet light in MEMS devices.

The method of formation of an electret, techniques to probe its properties and measurements of various parameters are depicted in Figure 3.

## Mapping of charge inside the electret

In the methods discussed so far, i.e. measurement of surface charge, TSDC and photo-depolarization, information about total charge stored, phase transition temperature and stability of electrets is obtained. The problem of determining spatial distribution of charge inside the electret still remained. Electret charge-mapping techniques have been developed with the help of newly developed techniques such as LIMM, LIPP, PEA and PIPP. Scanning of charge profile of an electret foil across its thickness has become possible with a resolution of the order of 1 micron.

## Laser intensity modulation method (LIMM)

In LIMM, an electret is exposed to a modulated light beam or a thermal wave, which creates a non homogenous deformation of the system<sup>6</sup>. The diffusion of heat inside the material leads to thermal expansion and changes in the temperature-dependent physical properties

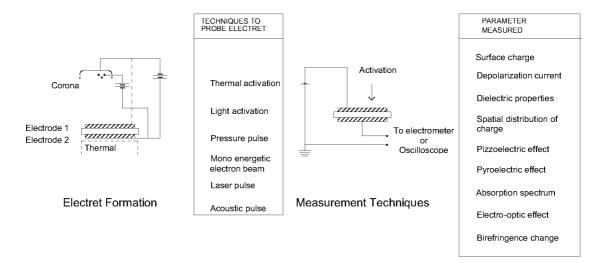


Figure 3. Electret formation, method of activation, measurement techniques and parameters measured.

of the materials like dielectric permittivity, polarization, etc. A signal is generated in the external circuit, giving information about the spatial distribution of internal polarization across the thickness of the electret foil. The LIMM is well suited for very thin samples. The modulation frequencies can be varied from 100 Hz to 100 kHz.

#### Laser-induced pressure pulse (LIPP)

In the LIPP method, a short Nd: YAG laser pulse of energy 1 to 10 mJ traverses through the samples. The pressure pulse moves the trapped charge in the poled dielectric relative to adjacent electrodes, thereby modifying the internal electric field, and a current is induced in the external circuit.

#### Pulsed electro-acoustic (PEA)

PEA uses an acoustic pulse in place of a laser beam. The acoustic pulse modifies the internal electric field causing perturbation in the charge. A pressure wave signal is generated giving the polarization profile of the electret. This method can provide information on rapid evaluation of charges as well as dipolar distribution under fast varying voltages. Transmission of pressure signal is so rapid that it takes about 1 µs to transmit across a 2 mm sample.

#### Piezoelectric-induced pressure pulse (PIPP)

A piezoelectric transducer is used to generate mechanical force resulting in a pressure pulse across the sample. It is analogous to Kerr effect observed in optics for transparent dielectrics, but here it is applied to a non-transparent sample to characterize space charge profiles. The evolution of space charge profiles can be scanned to a good sensitivity. The PIPP method is used to reconstruct the three-dimensional charge distribution in electrets.

#### Electret applications

An electret when exposed to either a pressure wave, a thermal wave or a mechanical distortion, a light wave or a voltage pulse, produces signal in the external circuit. It can therefore be used to sense temperature, pressure, light, sound as well as electric signals. Developments in electret technology have led to commercially available electret devices, ranging from sensors, transducers and air filters to radiation dosimeters. Most devices need neither external power supply not battery during operation. The important criterion is their long-term charge stability, besides requisite material compatibility.

#### Electret sensors

Earliest applications of electrets were in xerography and electro-thermography as light and temperature sensors,

respectively. A photo or thermo-sensitive corona-charged polymer film coated on a substrate, when exposed to print media gets depolarized selectively and electrostatic images are formed. Using electrets, polarizability-suitable materials have been developed as infrared sensors, heat scanners and micro calorimeters. Fast pyroelectric sensors of polyvinyledenefluoride (PVDF) and ceramic composite electrets are found more suitable for strategic and other applications such as in burglar alarm. Current trend is towards development of large-scale pyroelectric arrays based on integrated-circuit technology on silicon substrate for traffic vision aids at night<sup>7</sup>.

An ECM is a pressure sensor having a moving electret diaphragm made of polymer film sandwiched between two electrodes. When sound wave is incident on the diaphragm, its movement alters the distance between two electrodes and capacitance of the device changes, producing voltage signal in the external circuit. Such microphone made of non-polar polymer like polytetrafluoroethylene (PTFF) commonly known as Teflon, became industrialized in early 1970s. The ECM is an eminently successful electret application in the telecommunication industry today. Teflon and its copolymer teflon-AF are still the best materials for ECM. A poled piezoelectric film of PVDF is another promising polymer used as diaphragm in electret microphone. Mechanical bending of diaphragm due to incident sound wave results in induced electric charge on the electrode. Both these configurations are being used in ECMs. A back-plate electret microphone configuration has a thin electret film of non-polar material like teflon or a piezoelectric material like PVDF coated on the back electrode, with a freely suspended diaphragm made of a conventional polymer such as polyethylene.

The sensitivity of an electret microphone is expressed as

$$S = \alpha E_0 / d_0 \sigma, \tag{2}$$

where  $\alpha$  is the proportionality constant,  $E_0$  is the electret charge potential,  $d_0$  is the distance between the electret and electrodes and  $\sigma$  is the stiffness of the diaphragm.

Improvement in heat resistance property of ECMs has been achieved in back-plate electret using the annealing process, which controls crystallization. Desirable material properties for electret microphones are low charge transport, high concentration of deep traps for ions and electrons, a high glass or crystalline transition temperature, high sensitivity, proper charge selectivity and low vapour absorption.

Acoustic impedance of electrets of certain copolymers like polyvinyledenefluoride: trifluoroethylene (PVDF: TrFE) is found to be comparable to those of water and blood, which makes them useful for underwater as well as biomedical applications. As active underwater sensors, novel application of such transducers in camouflaging

submerged objects and in the biomedical field, as bloodflow monitors have been conceived. A needle-type hydrophone using nano-composites of lead zirconate titanate (PZT) in PVDF: TrFE shows enhanced piezo-electric coefficient and good sensitivity for ultrasonic detection with higher signal-to-noise ratio. Computer codes that enable pulse compression and result in significant improvement in noise performance for no increase in bandwidth against standard maximal length pseudo tandem binary system are being developed. Useful frequency range of piezo polymer hydrophones has been increased to 100 kHz.

#### Electret actuators

Actuators are energy converters, usually converting electrical energy into mechanical energy. A see-saw-type switch of polymer electret film was demonstrated in 1970s. An electret electrostatic relay that uses much less driving energy than conventional electromagnetic relays has been proposed. Such relays are becoming practical with the advancements in flexible thin silicon dioxide electret micromachining techniques. One of the most promising applications of electret relay matrices is in premises information distribution system (PIDS) for controlling various functions in a building. Electret relay matrices are also being tested for telecommunication processing and transportation information highways. Application range of such actuators is extremely wide and has been growing steadily. Silicon compounds and non linear optical polymers have displayed electret phenomenon and can be tailor-made into nano-composites for use as micro-actuators in artificial muscles and tiny intelligent robots for internal inspection. Once developed, an electret micro-actuator would have application in medical prosthesis.

Electrets as lubricants enhance corrosion resistance of machine parts. Billions of microscopic Teflon spheres charged electrostatically and suspended in a high-grade lubricating oil make sol-electret. The spheres get distributed evenly due to dominant repulsive forces. Such solelectret as a lubricating interface between a rotating spindle and stationary contact leads to improved performance of bearings. A weak electric field in the metal polymer electrets interface is seen to provide several-fold reduction in the wear and tear in comparison to conventional oil. Besides acting as a lubricant and corrosion resistance medium, it can offset adverse electrical charge that originate in AC power supply in homes and is known to improve the sound quality of audio systems.

#### Electret filters and dosimeters

The first application of electrets leading to a patent was for an air filter in 1929. Airborne particles are a cause of serious health problems. It is necessary to develop simple and reliable filters/sensors for detection and control of air pollution. Use of electrets in filters is proving ideal due to their permanent electrostatic charge. Desirable properties for electret filters are high dielectric and mechanical strength as well as high volume resistivity. Electret composite filters with electrostatic charged fibres behave like mini capacitors, with one side of the fibre being charged negative and the other side being positive. The medium as a whole is neutral. Dust particles are attracted towards the filter and get deposited on the fibres leaving more space between the fibres for flow of air. Such electrets can be used as respirator filters and in desktop cleaning applications, where low resistance to airflow is essential. With increasing dust load, electret filters have shown high collection efficiency and lower pressure drop owing to electrostatic force on the surface. Electret fine fibres of non-polymer polymeric materials were introduced as substitutes for high efficiency particulate air (HEPA) filters used in nuclear fuel facilities<sup>10</sup>. HEPA filters have the capability to remove atmospheric particles of up to 10 microns (PM10).

Electrets can detect radioactive pollution in the air. Electret dosimeter has been designed for measurement of low and high energy radiation in the atmosphere. It has an ion chamber with an electret positioned at its bottom surface. Electret charge or surface potential is measured before and after the air is sucked inside the chamber. The rate of change of charge on the electret due to ionization caused by radiation divided by the time of exposure gives the radiation level. Initially proposed for measuring radiation leakage in nuclear plants, electrets have come into commercial use for indoor radon monitoring as well as airborne tritium and  $\alpha$ -particles in the environment. In a radon monitor, α-particles from radon ionize the air and the electret serves as a sensor for measuring ionization. Radon is a naturally-occurring radioactive gas emitted from the soil and is practically present everywhere on the planet. Its concentration is highest in regions where granite or shale is present. Not only outdoor but also indoor radon gas exposure is found to be injurious to health. A study conducted in USA (Iowa Radon Lung Cancer) has exposed significantly high risk factors of radon, specially for housewives. Electret dosimeters are handy and can be put in the pocket to find the dose rate exposure to the body. They can be fixed on the ceiling or walls and left for 1 to 3 h to find the radiation level inside a room. They can be designed for a large-scale survey as well. Rad Elec Inc. has commercially introduced compact and costeffective E-PERMs (electret passive integrated ionization systems) for this purpose.

Electret disinfectant equipment has been proposed for sterilizing and operating rooms in hospitals. Electret filters were also suggested for incorporation in smoking devices, so that tobacco smoke passes through it prior to entry into the lungs of a smoker. Future applications of electret in controlling pollution caused by automotive combustion and in chemical, metallurgical and electronics-related industrial processes are promising. Commercial electret air filters used in facemasks, vacuum cleaners, air conditioners, compact radon dosimeters and room air cleaners are already available in large numbers in the market.

# Electrets in energy sector

Electrets are increasing being prepared from thinner materials using processing techniques that consume less energy. Electret devices require no external battery to operate and thus save energy. Their application in the power sector as a source of electric field had developed early. Using microfabrication techniques, electret microswitches are ideal for devices requiring intelligent control. Electret studies have been reported for monitoring of the performance and aging in high-tension cables made of polyethylene, in power transmission. Application of electrets in hot gas clean-up systems for power generation using advanced technology such as integrated gasificoal combustion is another challenging proposition. Hot-gas electret filters would require materials in which charge is stable at high temperatures of the order of 300°C. Ceramic electrets as hot-gas filters are expected to improve the performance, while reducing the cost of operation and thus conserving energy.

Use of electret filtering property in liquid medium has been made in electrodialysis. It is an ion-separation technique that employs an electrostatic field produced by electrets. It can be used for such diverse applications as kidney dialyser, desalination of ocean water and solar pond research. Major breakthroughs are expected through availability of appropriate materials for such membranes.

#### Advent of MEMS technology

The last century has bestowed the twenty-first century with some directions for future research, and one of them is MEMS technology. This technology has become possible because of developments in microelectronics. It aims at development of products capable of performing a greater variety of functions such as mechanical, optical and biological, besides electrical in compact light weight designs, integrated on microchips. Microgears, micromotors, microactuators, micropumps and microswitches have been fabricated using MEMS technology. What is MEMS technology and how its impact is being felt in electret research are discussed below.

#### More about MEMS

It is a technology where micro-machines are embedded below the surface of a microelectronic device. By the end of the twentieth century, microelectronic devices with ultra large-scale interaction containing more than ten million transistors and capacitors on a chip, smaller than a fingernail, became possible. Micromachining techniques have been introduced to produce miniature mechanical components on a chip. Such microfabrication of moving components involves the use of many different materials than those used in microelectronics. Fabrication techniques are similar to those used in producing integrated circuits on chips. Photolithography, chemical vapour deposition, ion implantation and diffusion can be adopted for three-dimensional shapes of MEMS. As the MEMS are three-dimensional structures, there is more complexity in their design and packaging, thus requiring thorough knowledge of mechanical engineering and other disciplines.

Fabrication of MEMS is radically different from traditional machining developed through industrial engineering and require knowledge of molecular physics, molecular biology, solid state physics, materials as well and chemical engineering. Their manufacturing philosophy involves design of controlled deposition and etching steps with the objective of getting high-quality miniature electromechanical devices. The entire unit can be contained in silicon chips of size less than 0.5 mm  $\times$  0.5 mm. Materials are vital in micromachining and designs require knowledge of solid state properties and their special machining conditions. In design and manufacture of biosensors, molecular biology is intimately involved.

# Emerging electret technology applications

Recent developments in MEMS have attracted a great deal of interest in the development of electret devices on a microchip. The first attempt to use silicon micromachining for electret microphones was made by Sessler  $^{11}$  in 1984. A dramatic reduction in size of electret microphones up to 300  $\mu$  has been achieved recently using spin-coated Teflon-AF or PVDF film on silicon dioxide.

The application of MEMS in electret microphone research has demonstrated several advantages besides compactness and miniaturization, such as better phase control, ability to integrate electronic circuits, impedance matching, etc. The scope of application of electret sensors has broadened significantly with the advent of MEMS technology. Electret optical sensors that can play specific medical functions such as detection of onset of heart attack, ovulation, polyps and non-invasive imaging of internal organs are proposed. Insect-like robots of biocompatible materials can be developed to travel inside the human body for detection and cure of malignant tumours and applications such as *in situ* drug delivery and photochemotherapy.

A three-microphone digital system to improve sound localization ability of a deaf or deaf-blind person<sup>12</sup> has

been demonstrated using miniature electret microphones. The laboratory prototype uses cross-correlation algorithms for determination of time and phase difference between three micro-phase signals for real time coding of directions of sound sources. The device is so compact that it can be mounted on the eyeglass of a disabled person. Applications of such breakthroughs would be growing at a fascinating rate. Future electret MEMS devices in medical and other sectors are shown in Table 1.

## Challenges in materials research

Electrets have thrown greatest challenge in materials research for a wide range of applications. In the past, the shift in focus of electret research was driven by developments in materials. To begin with, waxes and resins were the only electret materials until 1950s. Inorganic dielectrics, aromatic hydrocarbons and polymeric materials were introduced in the late 1950s and 1960s. Studies on non-polar polymers, ceramics and biomaterials began in 1970s. Doped polymers and blends of different polymers have been investigated with the objective of understanding their structures. Studies of electric poling in polycrystalline ceramics, which align internal dipoles of the crystallites, and their piezoelectric or photo-ferroelectric properties have continuously led to development of new materials. Several new polymer composites, pyroelectric and piezoelectric materials have been introduced in 1980s. Tailor-made compositions of composite polymer

Table 1. Emerging electret MEMS applications

| Table 1. Emerging electret MEMS applications |   |  |  |  |
|--|---|--|--|--|
| Biomedical and health sectors                | Disposable blood pressure monitor Heart pacemaker Catheter tip temperature sensor for detection of onset of heart attack and ovulation Pointed drug delivery system Artificial muscle and veins Detection of polyps Kidney dialyser Fibre optic sensors for endoscopy |  |  |  |
| Telecommunications industry                  | Hearing aids Microhydrophones Cellular phones Sound localization aid for deaf-blind persons Optical electret microphone Laser scanners Holographic storage displays   |  |  |  |
| Building and transport sectors               | Premise information distribution system Automatic room light controller Touch switch Floor sensors and impact sensors Personal verification systems Pyroelectric array detector for night vision Gas flow meter Lubricants  |  |  |  |

ceramic, polymer silicon and nonlinear optical materials using sol gel and spray pyrolysis techniques have been the subject of research in the 1990s. Piezoelectric, porous polymers, electroceramics and silicon-based microsystems are the electret materials of 2000s. In the last 50 years electret search for materials has covered a long journey; from carnauba wax, advanced polymer–ceramic composites, nonlinear optical, porous and hybrid piezoelectric polymer thin films to MEMS. Decadal focus of materials studied for electret polarization is indicated in Figure 4. In the following paragraphs, developments in a prominent category of materials are summarized.

# Non-polar polymers

Non-polar polymers are low dielectric constant and low dielectric loss insulating materials. Because of their insulating properties and flexibility as well as ease in processing, such polymers have been a subject of electret studies since 1960s. It was found that charge stability of non-polar polymer electret films is exceptionally high. Teflon has proved to be a good electret material for application in ECMs and radiation dosimeters. Emergence of thin film preparation techniques in 1970s had

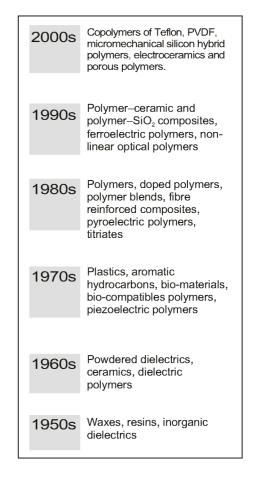


Figure 4. Materials focus of electret research.

#### Electret research in India.

From the very beginning, electret research in India was pursued with twofold objectives: (i) development of human resources, and (ii) search for new advanced materials. Bhawalkar started electret research in India at the University of Sagaur in early 1950s (ref. 21). Initiated by Bhawalkar.s students two centres of electret research grew more rapidly than others, one at the Indian Institute of Technology (IIT), Delhi (Pillai) and the other at M.A. College of Technology, Bhopal (Bhatnagar). From the very beginning, one of the goals of electret research in India was to search for new advanced materials to understand the polarization mechanism in them, for their possible applications in devices. Some of the earliest studies were made on thermoelectrets and magnetoelectrets of different types of waxes. Photoelectrets were introduced in the early 1970s (ref. 22). Early studies focused on organic photoconductors and biomaterials which could store charge for a longer duration.

Thermally stimulated depolarization current (TSDC) measurements were started at IIT Delhi in 1971. Electrets of different materials were characterized for applications in electro-photography, electro-thermography and X-ray dosimetery. During 1970s and 1980s, new groups in the country were nucleated at other places and electret research was being actively pursued at IIT Delhi and universities of Sagaur, Bhopal, Jabalpur, Tripura, Roorkee (now IIT) and other places. Major thrust of electret research has been on photoelectret studies in organic and inorganic dielectrics as well as thermoelectret studies in polymers, blends, polymer composites, piezo and pyro-electric materials, bio-polymers and electro-optic materials  $^{23.25}$ . A variety of natural and synthetic biopolymers such as enzymes, polysaccharides, glycine, haemoglobin,  $\beta$ -carotene, folic acids, dextrin-polysaccharide, vitamin D, ergosterol and kidney stones have been studied (Table 2). Dielectric properties of biopolymers are greatly influenced by bound woter molecules present in several layers. A study on photo-polarization in  $\beta$ -carotene, a biologically important member of C44 carotenoid occurring in both plants and animals, showed production of high charge densities in excess of 10  $\mu$ C/cm². Both its isomer forms,  $\epsilon$ /s. / rans, were investigated to study the structure correlation of polarization. The  $\epsilon$ /s form retained high-density polarization for reasonably longer time due to dipolar alignment, a property correlated with light sensitivity of memory effects of retinal systems in vertebrates. Electret applications have been proposed as biocompatible implants for heart pacemaker and detection of onset of heart attack.

In 1990s, opto-electronic interaction in nonlinear optical and piezoelectric polymer composites has been studied for developing tailor-made nano-materials. A study of PZT-based epoxy resin composite electrets using optical fibre sensor for laser light transmission has shown that micro bending due to heating results in intensity modulation and can be used as a tool not only for the study of polarization but also as a temperature sensor. In another study, a MEMS vibration sensor. As been tested in the laboratory using transparent thin films of barium titanate with donor/acceptor composites.

However, with changing focus, the infrastructure needs for materials processing have become substantially high and many of the centres nucleated earlier have not sustained for want of materials and manpower inputs. The electret research, which could flourish in the country as low-cost applied research by sharing the materials characterization facilities, has opened immense possibilities in development of tailormade materials for MEMS applications and requires a new thrust.

Table 2. Materials studied for electret research by different groups in the country

| Organic dielectrics and photoconductors | Biomaterials           | Polymers and their blends   | Polymer ceramic composites            |
|---|------------------------|-----------------------------|---------------------------------------|
| Naphthalene                             | Glycine                | Polyethylene terephthalate  | Polyvinyledine fluoride               |
| Anthracene                              | β-carotene             | Polytetrafluroethylene      | Barium titanate                       |
| Pyrene                                  | Folic acid             | Polypropylene               | Lead zirconium titanate               |
| Ferrocene                               | Dextrin-polysaccharide | Polymethamethylacralate     | La-doped lead titanate                |
| Acenaphthene                            | Haemoglobin            | Polyethylene, polycarbonate | Fibre-reinforced PP                   |
| Shellac wax                             | Vitamin D              | Polyoxymethylene            | Ba TiO <sub>3</sub> : PVDF composite  |
| Epoxy resin                             | Ergosterol             | Cellulose acetate           | Polyimide: lithium niobate            |
| Phenolic resin                          | Enzymes                | Polyvinyl acetate           | Anthracene-doped PMMA                 |
| Cadmium sulphide                        | Kidney stone           | Polyimide, polystyrene      | Rare earths-doped Ba TiO <sub>3</sub> |
| Lead sulphide                           | Bone                   | Polyacrylonitrile           | Mica-loaded PVC                       |

significant impact on electret research. The TSDC studies on polymeric thin films were made to get information on their structural, phase and glass transitions.

New forms of non-polar materials as copolymers and porous materials have been developed, which show exceptional stability for future electret devices. MEMS electrets of submicron thin layer of PTFE became possible as a result of materials science research. A copolymer of PTFE and perfluoro-2 dimethyl 1,3 dioxole as Teflon-AF exists in liquid form and can be spin-coated on the electrode in submicron thin layer with better adhesion on electrode materials than Teflon. It has porous structure

and charge is stored in voids of free volume and interfacial boundaries. Another advantage is that it is amenable to lithographic chemicals. Charged by electron beam injection from back-lighted thyratron, the polarization is known to be retained for as long as 10 to 100 years. It appears ideal for MEMS devices such as gyros, accelerometers and pressure transducers. There is need to prepare a database on dielectric and electret properties of different nonpolar materials for giving a boost to applied research.

#### Piezoelectric materials

Ever since Jacques and Pierre Curie discovered the ferroelectric effect in Rochelle salt way back in 1880, the field of applications of ferroelectric materials has been growing. Ferroelectricity in single crystals was observed in 1920s, but it was the discovery of ferroelectricity in polycrystalline ceramics like barium titanate<sup>13</sup>, that has led to several new possibilities. Ferroelectric ceramics are non centrosymmetric polar materials and the dipoles present in them are randomly oriented. Electrical charging or poling process aligns the dipoles. Induced polarization responds to changes in thermal and mechanical stresses resulting in pyroelectric or piezoelectric responses. Such piezoelectric materials have found applications not only in microphones, but also in other electromechanical transducers and actuators<sup>14</sup>.

Following the observation of piezoelectricity in a polymeric material, namely PVDF in 1969, electret transducer applications using films of different thicknesses and crystallization forms were given a boost. A number of other polymer and ceramic compositions have since been investigated for their piezoelectric behaviour under different conditions of poling. So far, PVDF: TrFE is the only material that has been found suitable in commercial devices but search is on for others. Polymers are flexible and level of induced stain can be high in their spectral response<sup>15</sup>. On the other hand, ceramics have good piezoelectricity; however, they do not have desirable dielectric properties and are rigid. As a result, a new class of materials as a combination of copolymer and ceramic composites having higher electro-mechanical coupling coefficient, higher critical temperatures, are easily polarizable and that can be produced by low energy-consuming sol gel and solid solution methods is developing.

The piezoelectric coefficient of composite materials can be as high as 600 pc/N, compared to PZT with 220 pC/N and ferroelectric polymers with 30 pc/N. They make ideal electro-active polymers (EAP) for applications ranging from infrared sensors, actuators, electro-optic modulators and 'smart' sensors, and are proving superior to shape memory metal alloys. PZT replaced barium titanate; and it is now being replaced by lanthanum-doped lead zirconate titanate (PLZT). Ferroelectric relaxor ternary system comprising PZN-PFN-BZN com-

posites<sup>16</sup> has shown reasonably good mechanical properties for application in multilayer ceramic capacitors and exotic dielectric behaviour. Further investigations on electrical and mechanical response of piezoelectric polymers and their ceramic composites, modelling of their nonlinear response and development of analytical tools for possible biomedical applications are the challenges to overcome.

## Nonlinear optical materials

Another category of electret materials are nonlinear optical materials. Certain polymer ceramic composites show flexibility of preparation, ease of tailoring their properties for desired applications and have demonstrated second-order nonlinear optical effects. Electric optical coefficient of most polymers is low, whereas ferroelectric oxides have high electro-optic coefficient but are difficult to grow as single crystals. Compared to single crystals, ferroelectric polycrystalline ceramics are generally opaque. However, discovery of optical transparency in PLZT systems in the late 1960s led to new possibilities. Doping with lanthanum in PZT resulted in producing transparency due to reduced anisotropy, which is found to be a function of the ratio of lanthanum and zirconium titanate. Manifestations of such optical nonlinearities are harmonic generation and refractive-index modulation.

New developments and breakthroughs using sol-gel processed electrets of glass:polymer composites showing femtosecond optical gate studies and other optical devices have been achieved by simultaneous application of electrical and optical fields 17. As guest-host composites, nonlinear optical materials are emerging as the most demanding materials for a wide variety of electret applications. Optical polymer waveguides can be structured in the plane of a thin polymer layer by selectively poling the waveguide areas, which acquire different refractive indices. By using poling fields perpendicular or parallel to the layer, transverse electrical or transverse magnetic waves can be guided. Such a device can be used in developing prototype of interferometers and direction couplers. Nonlinear optical properties of SiO<sub>2</sub>-polymer composites are of interest in developing an electro-optic switch for automatic room-light controllers in buildings. Photo-refractive property of doped ceramics which act as nonlinear optical polymers, needs to be further investigated in terms of new materials synthesis for applications in dynamic charge storage, image processing and holographic displays.

#### Porous polymers

It is seen that amorphous or crystalline polymers when stretched, show voids and behave like porous materials. These interstitial sites provide ideal locations for trapping

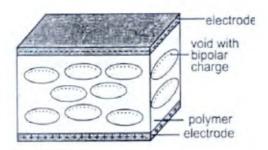


Figure 5. Trapping of charge in the voids for a porous material.

of electric charges (Figure 5). Such materials have demonstrated increased electrical and mechanical strengths. Electret behaviour study of stretched polypropylene (PPS) conducted by Goel et al. 18 in 1981, indicated that a discontinuity between crystalline and amorphous boundaries due to the presence of voids was responsible for reducing charge mobility and stiffness enhancement in comparison to melt pressed polypropylene (PP). Biaxialoriented thin polypropylene films with multiple air-gap layers or cellular structures have recently been prepared as electromechanical films (EMFis). By corona-charging during manufacturing<sup>19</sup>, this film has been tested as a sensor. An external force on the EMFi surface, changes the thickness of air voids and charge is generated at the electrodes. Thus, porosity is proving to be a promising property for electrets in large-scale sensor and actuator applications. When used in shoe soles, it helps in monitoring of the pressure distribution during walking. Placed under conventional flooring tiles, it could be used for recording of the footsteps and other movements on the

The concept of double layer sandwich of one softer and one harder layer with an electret has been introduced in polystyrene (PS) and PP films as well as PTFE and PPS films. These polymer foam electret transducers are found suitable for measuring finer movements in airborne ultrasound devices for application in industry as well as respirator detector in the biomedical field. A flat sensor placed between the patient receiving drug and the supporting mattress<sup>20</sup> can monitor the effect of the drug on respiration. In nature, porous materials exist in many forms in plant leaves as well as in living beings. In fact, porosity in the leg bones of a horse is known to give it immense strength. Most biomaterials are porous, having water-molecule polarizability. Importance of porous materials in electret research is being recognized and may reveal entirely unknown features.

# Silicon hybrid compounds

Silicon dioxide, gallium arsenide and silicon nitrides are extensively used in semiconductor devices and microelectronics. These silica compounds have been studied for charge storage and form promising electret materials. It is seen that nonlinear electro-optical effects can be generated in silicon oxide layers by electron beam charging. Such electrets are more stable in comparison to thermally poled electrets. Silicon dioxide contributes not only to the total electrical capacitance, but also to the thermal resistance of a sensor. The output current is hardly influenced by small changes in the temperature. An electret optical microphone in which vibrations of the membrane produce a varying electric field modulate the amount of current flowing in the external circuit can be integrated with FET on the same chip. Optical silicon microphone is thousand times more sensitive than condenser microphone, and provides a solution to short lifetime problems of humidity-sensitive microphones in theatres.

A MIS (metal-insulator-semiconductor) solar cell has been proposed using layers of PVDF-TrFE copolymer or non-polar Teflon-AF as active material between silicon dioxide layers as the absorbing coating at the interaction of the mesh in the upper contact. The spherical coating provided an area greater than that occupied by the upper electrode and absorbs the radiation. The current-voltage characteristics of coated electret solar cells have been measured and show promise for further research. Current traverses through the external circuit due to difference in the electrochemical potential when metal electrodes are connected.

#### Materials for MEMS

In microelectronics, silicon is the base material. In microsystems, a substrate serves an additional purpose of acting as a transducer and becomes an active substrate material. Hence the scope of materials research has widened. A great deal of interest in use of different materials like metals, quartz, polymers and ceramics, besides silicon dioxide exists. Silicon nitride has many superior properties and is being considered attractive for MEMS. When LIGA (German abbreviation for lithography, electroforming and moulding) process was developed, polymethamethylacrylate (PMMA) became the optimal choice for photoresist materials. It also shows excellent chargestorage capability and therefore can become a promising material for use in MEMS electret devices. Advancements in MEMS technology have direct implications on electret research. However, the choice of materials for MEMS depends not only on the required parameter to be measured, but also integration of the material with the substrate. Piezoelectric ceramic materials are proving to be suitable for active electret vibration sensors and micro-accelerometers. PLZT has been used in a number of novel MEMS devices due to superior electromechanical properties. Other polymers like PVDF and PTFE are becoming increasing popular for MEMS in transducers.

Research problems in this direction include integration of the electret film with the remainder of the processing steps. It is seen that the magnitude of piezoelectret coefficient is affected by film compression, grain size, phase boundary and substrate material. Development of intelligent robots would require a combination of strong muscles (actuators) and sensitive sensors (diagnostics). Improved performance requires materials with high fractured toughness, large actuation strain and inherent vibration damping, besides charge stability. If such functions can be integrated into the same material and are scalable to support MEMS technology, unique bio-MEMS with great potential are in the offing. They offer great challenge to materials engineers requiring multidisciplinary capabilities, as the design and manufacture of the sensor and instrument would require knowledge and experience in molecular biology besides the physical, chemical and engineering. The possibilities are immense.

#### **Conclusions**

One of the remarkable features of worldwide electret research has been the insight into dielectric materials; the other is the scope for applications. An electret is a low cost and low energy-consuming device. Products employing electrets have been put into practical use in almost all areas of life. Glimpses of electret applications in building, transport and automation industry, environment and health sectors are presented. Electret sensors of various kinds, electret actuators, electret air-filters and dosimeters are fully developed technologies. Use of integrated circuit technology for fabrication of electret transducer makes an attractive choice for applications in miniature hearing aids and lightweight handsets.

The drive towards miniaturization and integration is posing new challenge to materials research. Nonlinear electrorestrictive materials offer new applications potential for devices in sensors, medical diagnostic transducers, temperature sensors, three-phase holography, high-capacity thin-film memory devices and smart devices. Developments in silicon electret technology have continuously extended the fascinating world of MEMS devices. These can develop into artificial muscles and tiny intelligent robots for internal inspection in manufacturing systems as well as in medical prosthesis applications such as detection of onset of heart attack, ovulation, polyps and non-invasive imaging of internal organs.

In India, electret research had started early. The focus has been on basic materials research, understanding of charge production and its stability in dielectrics. With the advancements in materials processing techniques, the focus has shifted to preparation and characterization of new materials as well as development of nano-composites. Electrets continue to address multidisciplinary materials

research and applications in MEMS devices, requiring teams from solid-state physics, chemistry, engineering and biology. The challenge they offer needs nucleation of new groups and new directions in research.

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