ions and electrons in action*

D. N. BOSE**

It is indeed an honour for me to be asked to deliver the Prof. S. K. Mitra Memorial Lecture this year as I was a student of this Institute of which he was the Founder Director. Memorably I was in the audience when Prof. Mitra and Prof. S. N Bose were felicitated on being elected Fellows of the Royal Society. Prof. Mitra, as is well-known was a pioneer in the study of the Ionosphere and Radio wave propagation. The first experimental evidence of E layer first predicted by Heaviside and Kennely was obtained by Mitra and Rakshit in 1930. His seminal book 'The Upper Atmosphere' has been considered a Bible for researchers in the field.

Sisir Kumar Mitra was born in Calcutta in 1890 and joined Presidency College for his B.Sc in 1908. After a brilliant academic career at the University of Calcutta standing 1st in the M.Sc examination in 1912, he joined Prof. C. V. Raman at the IACS in 1916 and obtained his D.Sc in 1919. Thereafter he proceeded to France and worked with Prof. M. Curie and Prof. Fabry and obtained a second D.Sc. On his return in 1923 he was appointed Khaira Professor in the Department of Physics, Calcutta University. He formed an outstanding group for investigating the properties of the Ionosphere (named by Watson-Watt) through ground-based measurements. Unknown to Marconi it was the presence of the Ionosphere which allowed him to transmit signals across the Atlantic from Poldhu in Cornwall to Newfoundland. The ionosphere, it was discovered, consists of a plasma of ions and electrons formed by the sun's ultraviolet radiation, which reflects radio waves below a critical frequency.

\[ \omega_c = \left[ \frac{4 \pi n e^2}{m_e} \right]^{1/2} \]

where \( n \) = electron density and \( m_e \) = electron mass.

Using indigenously fabricated equipment Prof Mitra's group, which included Prof. H. K. Rakshit, Prof. J. N. Bhar and Prof. S. S. Baral, determined from \( \omega_c \) and polarization measurements, the properties of the ionospheric layers – the electron density, electron temperature and the magnetic field at these locations. This was a remarkable achievement, the data being later verified by rockets and satellites.

Apart from frontier-level research Prof Mitra was instrumental in promoting broadcasting in India, Calcutta being at the centre of such activities. He also established the Institute of Radiophysics and Electronics at the University of Calcutta in 1949 which remains a lasting memorial to him.

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**Electrons in Action**

The identification of the electron as a carrier of electric charge by J. J. Thomson, followed by the invention of the vacuum diode and triode by Fleming and de Forest respectively in the early 20th century, gave birth to the science of Electronics. At first a part of Physics, the rapid advances in Wireless Communication and Radar followed by the realization of Electronic Analog and Digital computers marked out a separate niche for the subject. The equipment used by Prof Mitra and his contemporaries were naturally based on vacuum tubes, which evolved to generate high power at high frequencies e.g. using the klystron, magnetron and traveling wave tube (TWT).

The invention of the transistor in 1947 closely followed by the Integrated Circuit in 1957 by Noyce and Kilby brought about a revolution which has made possible mobile phones, laptop computers, the Internet and Man's flights to the Moon – the substance of science fiction a few decades back. Truly there is no field of human endeavour including transportation, medicine, entertainment which does not depend on Electronics. 10 million transistors on a Silicon chip has become commonplace, with progress still following Moore's Law (Fig. 1) which predicted doubling of device density every 2 years. With miniaturization has come portability accompanied by a myriad of new applications – GPS is only one such example.

**Novel Gate Oxides**

As is well-known the MOS transistor is a building block of most IC chips. One of the limitations to continuing miniaturization of the MOS is that the oxide layer thickness has already decreased to around 10 nm. Any further decrease will lead to

- a) increase in leakage current
- b) tunneling
- c) dielectric breakdown.

One technique around this problem is the use of high κ dielectrics instead of the usual SiO₂. Since the oxide capacitance \( C = \kappa A/t \), where \( A \) are and \( t = \) thickness, a higher value of \( \kappa \) will permit the use of a thicker insulating layer. However the new dielectric must also have the excellent properties of native-grown oxide e.g. low interface state density, chemical compatibility, good morphology etc. Electronic requirements include high band gap, high band offsets, high dielectric constant. Extensive search has included the oxides and oxynitrides of rare-earth metals of which HfO₂ and ZrO₂ as well as mixed oxides. Gadolinium Gallium Garnet (GGG) have been found to be most suitable for SiGe as well as GaAs MOS devices.

**Ions in Action**

The realization has dawned of late that portable devices require portable sources of power. It is no longer enough to depend on the grid – batteries have become irreplaceable in modern electronics. The electric car also needs light weight, high energy density power sources to make it viable and popular. Batteries are based on the motion of ions which can store charge and release them when required, preferably in a completely reversible reaction. There are, as is well known of 2 types – primary and secondary.

Lead-acid batteries have been the mainstay of automobiles for almost a century but are notoriously heavy and have low output voltage and low power / weight ratio.

![Fig. 1. Moore's Law for Silicon IC.](image1)

![Fig. 2. Comparison of Battery Technologies – Energy density as a function of size vs weight.](image2)
Alternatives are the Zn – Cu, Ni-Cd, Ni-hydride and Li cells (Fig. 2). The latter is especially attractive for portable electronics due to its high output voltage ~ 3 V, high energy density and low weight. Hence the importance of ions in action!

**Microwave Electronics**

It is now well-recognised that Acharya Jagadish Chandra Bose was the first to generate microwaves and millimeter waves in the 1890s. He also invented a galena detector for radio waves. The unique quasi-optical properties of these waves were recognized only 40 years later when these proved vital for radar applications. He also modified coherers (metal-semiconductor contacts) as detectors of radio waves. In the 1960s new types of semiconductor microwave devices, such as Gunn and IMPATT diodes were invented and have now largely replaced vacuum tubes for low power applications. For communication purposes the microwave signals generated require to be modulated at high frequencies, this being achieved using Si p-i-n diodes.

Simpler alternatives to these p-i-n diodes based on chalcogenides with special properties were developed at the I.I.Sc Bangalore in 1977–78. The uniqueness of these switches lay in the fact that both threshold (TH) and memory-type (M) switches could be fabricated, depending on the material composition. These switches were invented by Ovshinsky in 1969 but their switching at microwave frequencies were first studied and patented by Bose.

These switches having a typical composition SiTeAsGe (STAG) are based on glass-forming material. Compositions near the edge of the glass forming regions can crystallise easily when heated and cooled slowly while compositions in the centre of these regions retain their amorphous nature. The former thus form Memory switches and the latter Threshold switches.

On the application of a small voltage to a TH switch, OFF state is obtained until a threshold voltage \( V_{th} \) is reached when a conducting filament formed thus dramatically lowering the resistance. With increasing current the filament diamenter increased at constant current density. When the voltage was removed the filamentary area reverted to its original amorphous state. M switch behaviour was similar till switching on, when a glass – crystalline transition occurred thus maintaining the ON state when the applied voltage was removed. The OFF state could be restored by the application of a voltage pulse which restored the glassy phase on sudden cooling.

The switches were formed by simple evaporation as thin films on metal substrates and unlike p-i-n diodes were bi-directional. Using a Gunn diode source and a crystal detector, these switches were mounted in a waveguide and could modulate the 8 – 10 GHz signal at frequencies upto 500 MHz. Both threshold and memory type operation was demonstrated. The advantage of memory type switches are that these are non-volatile and require no holding current.

**Fig. 4. Microwave loss vs operating current**

Microwave devices require to be tuned to desirable frequencies as a communication source. Fast tuning is required for strategic purposes in aero-space applications. These require tunable filters and oscillators which are based on ferrimagnetic resonance (FMR) in Yttrium Iron Garnet (YIG) single crystals. YIG is chosen because of its extremely low line width (< 0.2 Oe) and low loss which results in small spheres acting as high Q (> 10,000) microwave resonators. The resonant frequency \( f_r \) varies linearly with applied dc magnetic field \( H_0 \) as

\[
\frac{f_r}{H_0} = \text{const}
\]

The growth of single crystals of YIG is a challenging task as it requires flux growth at 1350 °C in Pt crucibles. These were grown in a major DRDO project by Kutty and Vasudevmurthy in the IPC Dept at I.I.Sc and fully characterised in the ECE Department by Bose and
Chatterjee. Tunable filters and Gunn oscillators in the X-band were fabricated and tested and the technology handed over to DLRL, Hyderabad.

**Plasma Deposition**

One of the major themes of this talk is Plasmas. An important application of Plasmas is in Semiconductor technology where Plasma deposition is an established method of laying down layers of metals or dielectrics on desired semiconductor substrates. Its principal advantage over conventional Chemical Vapour Deposition (CVD) is in the low substrate temperature at which this can be accomplished. This results in lower substrate decomposition for materials such as GaAs and lower out-diffusion from pre-fabricated devices.

Silicon Nitride (SiN\(_x\)) is an excellent dielectric which can be used for surface protection of semiconductor devices. It can be formed by CVD at 800\(^\circ\) C by the following reaction:

\[
\text{SiH}_4 + \text{NH}_3 \rightarrow \text{SiN} + \text{H}_2
\]

However the same reaction can be carried out at 450\(^\circ\) C using an r.f plasma whose purpose is to create highly reactive ionic species. The composition which controls the important properties such as dielectric constant, refractive index, resistivity and film thickness can be tailored by controlling 4 parameters:

i) Partial Pressure  
ii) Flow rates of reactants  
iii) Plasma power density (W/cm\(^2\))  
iv) Substrate temperature

Neural network modeling was used by Ghosh and Bose to develop response curves to demonstrate the variation of refractive index vs substrate temperature and pressure as shown in Fig. 5a). Similarly the variation deposition rate vs r.f power and gas flow rate is shown in Fig. 5b).

b) variation deposition rate vs r.f power and gas flow rate

From these studies the conclusions drawn were:

i) the deposition rate depends primarily on r.f. power  
ii) the refractive index depends on combination of gas composition, chamber pressure and substrate temperature.

**Ferroelectrics**

Ferroelectricity (FE) is a well-known phenomenon in which a solid displays spontaneous dielectric polarization which can be reversed on the application of an electric field \(E\). It was discovered in Rochelle salt as recently as 1920 by Valasek, in contrast with Ferromagnetism (FM) which was known by way of 'lodestone' to the Chinese 1500 years back. The name itself suggests an analogy with ferromagnetism but the principles are quite different. Whereas ferromagnetism depends on unpaired electron spin, ferroelectricity depends on the motion of ions so
that the centre of positive and negative charges are displaced from each other. This may occur below a Curie temperature in solids which then become non-centrosymmetric. The most well-known example is BatiO$_3$ discovered in 1945 which is ferroelectric below 120°C. In simple terms that there can be no polarization when the centres of positive and negative charges in a unit cell coincide. However at low temperatures, the system can reach a lower energy state when the two do not coincide, thus resulting in a built-in polarization. This is shown in Fig. 6.

There is considerable interest in using these properties to form non-volatile memories (FeRAMS) in chips. Ferroelectrics are usually insulators but some semiconducting ferroelectrics are known. Pal and Bose$^{17}$ found a new semiconducting ferroelectric Ga$_{1-x}$Ge$_x$Te for which the dielectric constant, Curie temperature, optical gap and resistivity could be varied by varying the Ga : Ge ratio. Fig. 7a) and b).

For memory applications square loop P-E hysteresis characteristics at room temperatures and a high Curie temperature are essential. This has been realised in Ga$_{1-x}$Ge$_x$Te as shown in Fig. 8. The material (for $x = 0.2$) showed a 2nd other phase transition with $T_c = 753$ K as shown. The resistivity, which should be $>10^{12}$ ohm cm, is however not as high as desired which would result in charge leakage.

**Multiferroics**

Ferromagnetism (FM) resulting from coupling between electron spins and Ferroelectricity (FE) due to charge ordering have till recently been considered to be mutually exclusive. However Pierre Curie$^{18}$ had predicted in 1894 that in theory there exists 13 point groups that allow both FE & FM. It was predicted theoretically by Dzyaloshinskii$^{19}$ and others but it was not till 1962 that this ‘multiferroic’ behaviour was observed by Folen$^{20}$ and thereafter almost forgotten.

In the last decade there has been a surge interest in these novel materials, prominent among which are BiFeO$_3$ (perovskite-structure), TbMnO$_3$ and YMnO$_3$. The properties of these materials are given in Table 1$^{21}$:

<table>
<thead>
<tr>
<th>Multiferroic</th>
<th>Dielectric constant</th>
<th>$T_c$ (0 K)</th>
<th>$T_N$ (0 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YMnO$_3$</td>
<td>20</td>
<td>920</td>
<td>80</td>
</tr>
<tr>
<td>TbMnO$_3$</td>
<td>30</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>BiFeO$_3$</td>
<td>100-150</td>
<td>1103</td>
<td>640</td>
</tr>
</tbody>
</table>

While BiFeO$_3$ is the most promising at the moment it is desirable to have both excellent FE and FM properties with high Neel temperature ($T_N$) and Curie temperature ($T_c$) in the same material. These multiferroics, which can be deposited in thin film Formby laser ablation, can have a number novel applications such as:

a) Electrically addressed Magnetic memory
b) Sensors and transducers
c) Electrically tunable microwave devices e.g. filters, oscillators and phase shifters.

d) Novel Spintronic devices e.g. (TMR) sensors and spin valves with electric field tunable functions.

e) Multiple state memory elements, where data stored both in electric and magnetic polarizations.

**Lithium Ion Batteries**

The first ionic conductor $\text{AgI}$, in which $\text{Ag}^+$ ions are mobile, was discovered by Faraday. Ionic conductivity is understood to result from the presence of defects (vacancies and / or interstitials) in solids and has been intensively studied. A large number of such conductors with mobile cations such as $\text{Li}^+$, $\text{Na}^+$ and $\text{Ag}^+$ or anions such as $\text{F}^-$, $\text{O}_{2}^{-}$ have been found. Among these, ones with high values of ionic conductivity ($\sigma = 10^{-3} - 10^{-1}\ \text{ohm}^{-1}\ \text{cm}^{-1}$) are called Fast Ion conductors or solid electrolytes. Prominent materials include:

- Ag ion conductors – $\text{AgI}$, $\text{RbAg}_{4}\text{I}_5$
- $\beta$ – Alumina ($\text{Al}_2\text{O}_3$)
- Yttria-stabilised Zirconia ($\text{Y}_2\text{O}_3 - \text{Al}_2\text{O}_3$)
- Oxygen ion conductors – Fluorites
- Lithium ion conductors $\text{Li}_2\text{SO}_4$, LiSiCON
- Glassy and Polymer electrolytes

Of these $\beta$ – Alumina ($\text{Al}_2\text{O}_3$) and Yttria-stabilised Zirconia ($\text{Y}_2\text{O}_3 - \text{Al}_2\text{O}_3$) exhibit high ionic conductivity only at high temperatures and hence are ruled out for battery applications, though these are useful for fuel cells. The presence of appreciable electronic conductivity in some materials is also a deterrent as it causes self-discharge. The advantages of Li ion batteries are:

i) Li is highly electropositive with an intercalation voltage 3.5 V relative to Li metal

ii) lies 3rd in the Periodic Table and hence has very low density and weight

iii) high energy density

iv) non-toxic, easily available and low cost

v) good cycleability

vi) low self-discharge

Thus Li ion batteries have captured 63% of worldwide sales in portable batteries.

At I.I.T Kharagpur, Mazumdar and Bose prepared a wide range of Li ion conductors such as $\text{Li Zn}$ germanates and vanadates and studied their ionic conductivity vs temperature at varying frequencies. Following Whittingham who first demonstrated the use of $\text{Li}_x\text{TiS}_2$ as the positive electrode, cells using the process of electrochemical intercalation of lithium into $\text{TiS}_2$ were fabricated. LiSiCON (LiThium SuperIonic Conductor) was used as the solid electrolyte and charge – discharge over 50 cycles demonstrated.

An interesting non-contact technique employed for studying ionic motion is through Nuclear Magnetic Resonance (NMR). The NMR linewidth is a function of nearest-neighbour interaction. In solids these are fixed in the lattice leading to linewidth broadening whereas in liquids where the nearest-neighbours are time-varying, the linewidth is narrow. This provides a method of examining liquid-like behaviour of Li$^+$ ions, which provide an NMR signal due to the presence of nuclear spin. The results of line-narrowing as the temperature is increased are shown in Fig. 10.

Lithium electrodes are chosen because of the intercalation properties present in layer-type materials. intercalation involves the insertion of extra ions into a crystal structure without any chemical reaction. Thus this a reversible process most commonly observed in graphite. For Li cells Lithium Cobaltate ($\text{Li}_{1-x}\text{CoO}_2$) is chosen as the cathode as it can accommodate Li ions between its layers. The anode is typically $\text{Li}_x\text{C}_6$. During charging Li$^+$ ions are driven by the externally applied electric field from cathode to anode while the reverse motion occurs on discharge, when positive current flows through an external load from cathode to anode. The electrolytes currently used are liquids or polymer (PEO-LiCF$_3$SO$_3$) complexes since solid electrolytes do not as yet have the required high
conductivity. An important requirement is the ability for repeated charge – discharge over at least 10,000 cycles.

Fig. 11. Lithium intercalation in Li$_{1/0x}$CoO$_2$

**Plasmonics**

Since this talk has Plasmas as a special theme I shall conclude with a glimpse of the newly emerging area Plasmonics$^{26}$. This deals with Plasmons, which are quantized excitations of electron density waves with characteristic resonant frequencies. These can be divided into

a) Surface Plasmons (SP) – quantized excitations at metal-dielectric interface with very short wavelengths at EM frequencies (Fig. 12a)

b) Localized plasmons (LP), which as the name suggest are plasmons localized e.g. at gold or other nanoparticles (Fig. 12b).

While in space the plasma frequency $\omega_p = (4\pi n e^2/mc)^{1/2}$

Surface Plasmons at metal-dielectric interface have a frequency $= \omega_p / \sqrt{2}$

Localized plasmons at nanoparticles have a frequency $= \omega_p / \sqrt{3}$

Thus at a metal-dielectric interface velocity of EM waves is reduced and hence at same frequency $v$, wavelength $\lambda = v/\nu$ is reduced.

Plasmons are closely connected with a large range of phenomena including optical absorption, Rayleigh scattering, Surface – enhanced fluorescence and Surface – enhanced Raman scattering (SERS). Localised plasmon properties have been shown to the intimately connected to Nanostructures and Nano – apertures. For example as shown in Fig. 13, the fluorescent wavelength depends strongly on the size and shape of Ag nanoparticles. Plasmonics has been employed to act as waveguides, switches and slot antennas.

Other applications$^{27}$ include Tunable Optical devices, Nanoscale waveguiding, Ultra-fast Photonic interconnects, high efficiency LEDs, chemical & biological Sensors. Associated photo-thermal effects can be used for destroying cancer cells.
Conclusion

The motion of Ions and Electrons play a leading role in modern technology. Prof Mitra showed that the ultraviolet radiation from the sun was responsible for creating the E layer which consisted of a plasma of Ions and Electrons. The presence of this Ionosphere was the reason that long distance radio wave propagation was possible. Plasmas generated in the laboratory have been shown to be very useful for low temperature deposition of dielectrics. Examples given from the field of Electronics include the march towards miniaturization of MOS devices, the basic component of ICs, using high alternative high $\kappa$ dielectrics. This is what keeps Moore's Law alive. Other examples given include microwave modulation using amorphous semiconductor switches and microwave communication using YIG-tuned filters and oscillators. Ionic motion is responsible for phenomena ranging from Ferroelectricity useful for non-volatile memories and Lithium Ion Batteries which are irreplaceable for portable devices. Most recently the new fields of Ferroics and Plasmonics have opened up, of which some examples have been given.

References

2. Wikipedia on 'Professor Sisir Kumar Mitra'
7. J. C. Bose, U. S. Patent. 775 840 (1904)
16. J. Valasek, Phys. Rev. 15 537 (1920); Phys. Rev. 17 475 (1921)