Dr S. A. Al-Jabbar

Experiment of High Temperature Superconductor

See review in Infinite Energy vol 79, July 2008.

Abstract

The present work aims at the preparation of filaments of bismuth powder/ epoxy resin and examined them to be high conductor with locally available material and tools following our technology comparing with Bourgoin method.

Three sets of bismuth filaments were prepared at different conditions and the current – voltage (I-V) characteristics measured by 2- probe system to examine the electrical resistance.

The first set samples ware prepared by cold work preparation process (at room temperature) using bismuth powder of < 50μm grain size and (0.1)g weight with epoxy resin (101Ay) and the hardner Hy 596 mixed at 3:1 volume ratio using electrophoresis technique with DC. voltage (0-800) V. Two (copper and stainless steel) electrodes oppositely headed immersed in the mixture 1mm apart with increasing the applied voltage bismuth filament was form with (1-50) mm length and DC. current flows (<0.1mA) for 15 min. After about 24 hours the filaments lost their conductivity due to the weak formation of filament structure.

The second set was prepared by hot work preparation process (at $271^{o}C$) using 1.0 g of bismuth mixed with 15ml of Hy 596 liquid insulator

and heating the mixture to bismuth melting point (271^{o}C) stirring at the beginning and keeping the mixture for 2hr.

Two brass electrodes immersed oppositely headed 1mm a part in suspension with applying (0-50)V DC. voltage for 15 min. The migration of conductor particles form as bismuth filament with (1.0mm) length following electric field lines.

The I-V characteristics differ between samples. 22 samples were prepared. The first 9 samples of bismuth filament showed linear ohmic behavior while the other 13 samples showed non linear ohmic conductivity.

The third set was prepared using 20g of bismuth powder mixed with 20ml of Hy 596 (insulator material liquid) heated for 45 min at 310^{o}C with continuous stirriring. The pair brass electrodes immersed in the suspension and 1kV DC. voltage was applied for 5 minute with 1MΩ resistance , after which the bismuth filament began to formed, 1mA DC. current flowed for 5 min to complete the formation process and annealing the bismuth filament to obtain a filament with 15 Ω and another 20 Ω resistance. The filaments prepared in this sets revealed the existence of high DC. conductivity reaching (3.5-4) A with very low resistance (~ 0.4)ohm.

The I-V characteristic of second set were examined after 5 months storage and showed obvious change in I-V curves. Four of these samples numbered (9,10,11,13) were irradiated with Gamma photons from ^{60}Co source with dose (14.3) Mrad for 40 days. The I-V test showed improvement in electrical conductivity for the samples (9,10,11), while sample (13) lost its conductivity completely after irradiation process.

Chapter 1

1-1 INTRODUCTION

The phenomenon of superconductivity was discovered by the Dutch physicist H. Kamerlingh Onnes and his assistant Gilles Holst in Leiden. They found that DC. resistivety of mercury suddenly drops to zero below 4.2 K, as shown in figure (1.1).

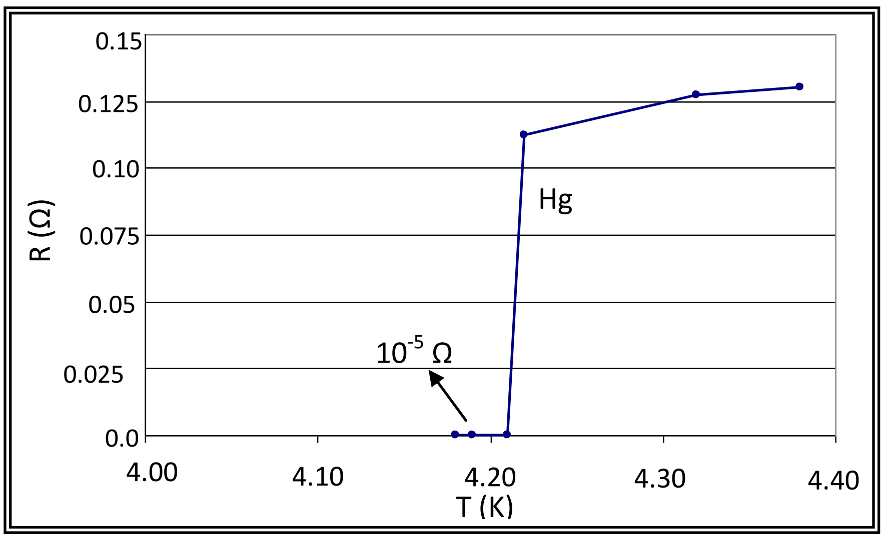


Figure (1.1) Experimental data obtained in mercury by Holst and Qnnes in 1911[1]

A year later , Kamerlingh Onnes and Holst discovered that a sufficiently strong magnetic field restores the resistivity in the sample as does a sufficiently strong electrical current[1].

Superconductivity is the complete disappearance of electrical resistance in various solids when they are cooled below their critical temperature. In order to reach this state three conditions must meet: the temperature must be below the critical temperature T_c , the magnetic field must be less than the critical magnetic field B_c and the current density must be less than the critical density I_c [2].

John Bardeen cooper and Shrieffer in 1957 were able to show theoretically that the superconductivity arose because electrons experienced an attraction interaction brought about by the vibrations of crystal lattice called BCS Theory[2].

Meissner and Ochsefeld discovered in 1933 that the material in the superconducting state exclude magnetic flux from their interior , exhibiting perfect diamagnetism under certain conditions. The property of magnetic flux exclusion in the presence of a magnetic field is called Meissner effect[3].

There are two types of superconductors; the first Type I (conventional superconducting) are very pure metals such as lead , mercury and tin . This type has a threshold or critical external magnetic field applied the magnetization cancels the applied field until there is an abrupt change from the superconducting state to the normal state[4] .

In 1986 Bendnorz and Muller discovered HTSC for Ba – La – CuO has T_c=35K this was the start of high temperature superconductivity.

Type II are high temperature superconductors such as ceramic metal oxides ($YBa_2Ca_3O_7$ (1987), Tc=(90-100)k and $Bi_2Si_2Ca_2Cu_3O_{10}$ (1988) T_c>105k). It is found that they have two values of critical magnetic field where below Hc_1 the superconductor excludes all magnetic field lines (diamagnetic superconductor) and above Hc_1 the magnetic field begins to penetrate and there is a complete penetration at Hc_2 where the material becomes normal between Hc_1 and Hc_2 ,the material is said to be in the mixed state[4] . In 1987 when ceramic was discovered as a high temperature superconductor, it was found that when it is cooled down to 100 K than to 10 K (Type I superconductor) it a greater potential for a technological application than the conventional superconducting metals. In spite that type II is called HTSC , they must be cooled to a temperature very low compared to room temperature therefore, they are limited in their applications[5,6].

In 1993 Schelling etal. discovered (HBCCO) has T_c=103K, and Chuet has discovered the system HBCCO has T_c>150K.

For many years, it was thought that all superconductors shared the characteristic properties common to the metal superconductors that were first discovered . It is now recognized , however , that there are different types of superconductors.

In addition to being classified TypeI (conventional superconductors) and Type II (unconventional superconductors); scientists refer to categorized superconductors by their dimensionality. Most are 3-D (bulk system) and some compounds like surface dopped $NaWo_3$ and some organic superconductors are 2-D like Li_2CuO_2 and single –walled carbon nanotubes have shown rare 1-D zero resistance room temperature superconductivity,[7,8,9].

Materials, known as “Ultraconductors ™” display room temperature resistance, have many orders of magnitude lower than the best metallic conductors. Their formation depends directly on a combination of material-specific factors especially the presence of electric dipoles (polar molecular groups attached to the long flexible chains of the polymer), and semi-liquid nature of the amorphous polymer medium. Examples of these materials include oxidized ataticpolypropylene (OAPP) and oxyacetylene. These materials might better be described as “Hyper conductors”. Meissner effect cannot be confirmed to this material yet[10,11].

Because electrical conductors attained new nano- technology revolutions and serious competition for the simpler and smaller of high quality devices, it is desirable to produce materials having a very high conductivity at room temperature with low cost and simpler method processing.

1-2 Room- Temperature Superconductivity

Finding room temperature superconductors is one of the most challenging problems in the science. It was theoretically shown that RT superconductivity cannot be realized within the conventional phonon-mediated pairing mechanism[12] . It has also been deconstructed that a polaronic effect can enhance superconductivity substantially[13]. But it is unclear whether RT superconductivity can be achieved within this mechanism . On the other hand , a theoretical calculation showed that superconductivity as high as 500K can be reached through a pairing interaction mediated undamped acoustic plasmon modes in aquasi-one dimentional electronic system[14].

Moreover, high- temperature superconductivity can occur in a multi–layer electronic system due to an attraction of charge carriers in the same conducting layer via exchange of virtual plasmons in neighboring layers[15].

If these theoretical studies are relevant , one should be able to find high – temperature superconductivity in quasi- one dimensional (1D) and or multi- layer systems.

An interesting theoretical and experimental patent study by Bourgoin in 1982 discloses a process for making bismuth filaments having room temperature superconductivity and his theory depends on a two fluid model . Forming a filament having (10-1000)^{o}A diameter opens a scientific area to study this phenomenon[16,17]

It is commonly believed that superconductivity cannot occur at room temperature (300 K , 27 ^{o}C) , but many researchers such as Bourgoin and Mourachkin and others believed that under suitable conditions , superconductivity can occur at or above room temperature and they ready to give guidelines on how to synthesize a room temperature superconductor[9,18,19].

It is used to think of superconductor as having apposite spin electron pairs and meissner effect, but recently many studies have shown new types of superconductor[20].

It is used to think of a superconductor as having apposite spin electrons pairs and a meissner effect , but recently many studies have shown new types of superconductivity[20].

There are ferromagnetic superconductor and ,Paramagnetic superconductivity[20].Also there is a new theory of superconductivity of unpaired electrons[21,22] or there is no need to have opposite spin momentums[23,24,25]. For room temperature superconductivity ; there are many researches of bismuth and carbon together because they have something common in electrical transition properties in small dimension systems[26].

1-3 Literature Survey

Superconductivity has been reported for Bi in 1953 by Chesterod and Jansand. where Tc=2.7 K for Bi III and 3.9K for Bi II by Brand and Ginzbary[27]. In 1964 Sauers , Jura and Jaggi studied bismuth and shown that bismuth becomes semiconductor when pressurized to above 10 Kbar at temperatures below 100 K [27] .

Carrol and Rabert in 1970 invented a heat transfer device which comprises in combination an electrical conductivity transfer unit and heat transfer having a plurality of filaments of bismuth , vanadium and zinc extending through insulated block. Petlier (model) heat transfer depends upon the existence of different work functions and conduction electron densities applying to different metals. If both conductors are in the same superconducting state, the current is confined to the surface so that the work function diffentials have no meaning . Thus it would appear that the removal of the resistance heating mechanism has also removed the petlier heat transfer mechanism . This invention depends upon extending the range of operation of superconductor materials to include normal ambient temperatures. The invention was achieved by using a series of heat transfer units of increasing heat capacities[28].

Thomson in 1980 had a method of making filament from a chemical collide suspension . He has taken externally fine metallic particles and suspended them in high dielectric medium such as epoxy resin, then heated the mixture to the metal melting point which is 271^{o}C of bismuth.

The only reason for doing that is to bring the mixture into molten or semi molten state. Then applied several thousand volts using electrical electrode high conductivity was observed. Then he refracted one set of electrodes as far as he wanted to get filament with length and cross section. When he took cross sections of mixture, he found little fibers going all over the place[29].

Bourgoin in 1982 published his invention which is a process for making electrical conductors in the form of filaments which exhibit properties of electrical superconductivity at ambient temperature or norml temperature. The process includes the preparation of a molten mixture of conductor (bismuth) and insulator (epoxy resin) materials . Then introduction of nearly homogeneous mixture between electrodes a cross which a voltage is applied causing fine filaments to be formed having a diameter within the range of 10 to 1000 ^{o}A . The filament thus formed gives almost no resistance to the passage of electricity there through at room temperature[16]. Figure (1.2) shows the I-V characteristic of bismuth filament formed by Bourgoin method.

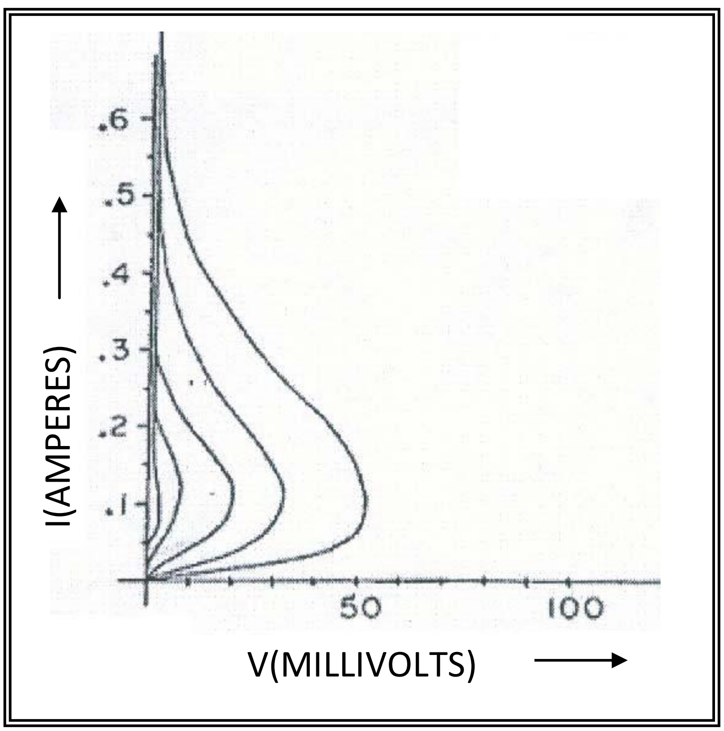


Figure (1.2): I-V characterization of Bismuth filament produced by Bourgoin method[16].

In his patent the information and result were not enough about magnetic properties of such filaments.

Wextzal and Hmmicklitz in 1991 have studied the superconducting properties of granular films but from well defined crystalline (rhombohedral) Bi cluster far above the percolation threshold. These granular films have been prepared by new method namely , by the in-beam preparation of metal clusters of a well- defined size L followed by a deposition together with a matrix atomic beam on a substrate at low temperatures. They found that these granular films are superconducting. This is the first time that superconductivity is found in small metal clusters. While the bulk material with the same structure is not superconducting . The superconducting transition temperature Tc strongly depends on cluster size L(L=2.5 and 40nm), which $T_c \leq 2K$ for $L \geq 20nm$, and T_c as well as the normal state conductivity б are strongly influnced by the surrounding matrix or adsorbed gas on the cluster surface . These experimental facts can be satisfactorily explained if assuming the occurrence of Bi surface superconductivity. It is attributed to a strongly enhanced density of states $N(E_f)$ at the cluster surface[30].

Dresselhaus and Black in 2000 repoted the effects exhibited as one gets smaller bismuth wires . When the sample size is smaller than the mean free path and de Broglie wavelength of the conduction electrons, then the electrons are quantum confined, and the electrons bands split into sub bands. Inter sub- band transition in bismuth nano wires were measured by optical absorption associated with the dimensional joint density of states of an inter sub- band transition in bismuth nano-wires. Bismuth nano wires were fabricated inside the pores of anodic alumina which serves as a host material. Since alumina is a wide- band gap semiconductor , individual wires are therefore electrically isolated. The optical absorption spectroscopy observed strong absorption in bismuth nano wires at ~ 1000 cm-, and is shown to depend on the wire diameter and on the polarization of the incident light. The absorption line shape, the decreasing frequency with increasing wire diameter, and the polarization dependence of the reflectivity, all indicate that this resonance is due to an inter sub- band absorption resulting from quantum – confinement effect[31]

Gupta et al., in 2001 reported studies of insulator superconductor transition (I-S) in quench condensed (at 1.8 K to 1.5K) bismuth films as a function of disorder (or film thickness) on a verity of substrates – amorphous quartz coated with Ge , and solid xenon condensed on quartz . The experiments were done in UHV cryostat equipped with reflection electron diffraction (RED).

(RED) studies show that Bi is almost amorphous and a transition from insulating type behavior to superconducting behavior as the thickness of the film is increased and cleared by the temperature dependence of sheet resistance R(T).

The transition temperature for Bi film of a given thickness is higher on substrates of higher relative permeability, and the normal state resistance is also higher, A 65^{o}A film on Xe, quartz and Ge has T_c of 3.8 , 4.2 and 4.42K, respectively . This shows that the conductance of a disordered film depends on the interplay between interaction and disorder[32].

Schmelzer etal. in 2002 presented a study of atomic bismuth clusters deposited between lithographically defined contacts with nanometer scale separation. The design of contacts is based on an appropriate application of percolation theory to the conduction in cluster deposited devices and to allow finite- size effects to be clearly observed. It is demonstrated both by experiment and by simulation , that for small contact separations the percolation threshold is shifted to extremely low surface coverges. The selected rectangular geometry ensures that the wire-like structures are formed close to the percolation threshold. In the experiment, a beam of bismuth clusters with a mean diameter of (60±10nm) is generated in an inert- gas aggregation source. Deposition onto a substrate with prefabricated contacts is controlled by a shutter. The NiCr/ Au contact is defined on a highly insulating and flat surface of 200nm SiN layer grown on a Si wafer, using a combination of standard optical and electron beam lithography (EBL) techniques . Atomic force microscopy (AFM) has been used to measure accurately the contact separations (ranging from 300 to 3200nm) and also to characterize contact less large- area samples consisting of cluster films deposited onto 3×3 mm piece of SiN. AFM image of the films with wide range of converges clearly show that Bismuth clusters strick to SiN surface on landing and donot diffuse and aggregate to form larger particles. During deposition a dc bias of 1.2V is applied across the contact and the current is measured as a function of deposition time[33].

Zhang and Zeng in 2003 prepared Bi and Sb super lattice nanowires which consist of a series of alternate nano dotes of two different materials. Bi /Sb super lattice nanowires were fabricated in anodic alumina membrances (AAM) by means of pulsed electrodepostion technique in a single ethanol path[38].

To investigate their properties; a clear electronic model of such system is thus imperative. The density of states of a Bi / Sb super lattice nonowire for each one dimensional sub-band and total density of states were calculated using the method developed by Lin and Dresse lhaus for nanowires in which the carrier energy obtained by solving the effective-mass Schrödinger equation and the density of states of each sub-band is calculated with Krong - Penney model. The minigaps in the total density may lead to change in the sign of the thermoporer thermial properties for certain energy ranges as the fermi energy varies , which indicates that the super lattic nanowire can demonstrate n - or p - type behavior by using the same dopant (Bi_2Te_3 / Sb_2Te_3) at 300 K[38].

Hick and Dersselhaus in 2003 have pointed out that low dimensional systems should have a better efficiency than their bulk counterparts owing to the enhancement of the thermal power by sharp of states and the reduction of lattice thermal conductivity by increased phonon scattering. Single crystal bismuth nano wires by pressure injecting molten bismuth into anodic alumina templates. By varying the template fabrication conditions , nano wires with diameters ranging from 10 to 200 nm and length of ~ 50 nm can be produced as shown in figure (1.3) . They presented a scheme for measuring the resistance of a single Bi nano wires using 4- point measurement technique. The nanowires are found to have

7nm thick oxide layer which causes very high contact resistance when electrodes are patterned on the top of the nanowires. The oxide is found to be resilient to acid etching , but can be successfully reduced in high temperature hydrogen and ammonia environments. The reformation time of the oxide in air is found to be less than the focused ion beam and is a promising technique for complete sputtering of the oxide without damaging the nanowires[35].

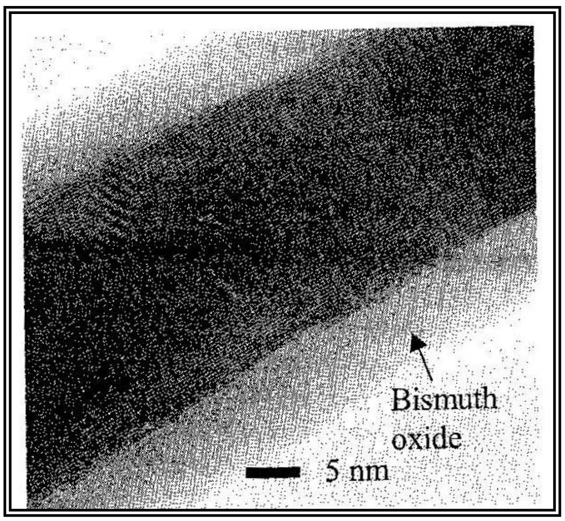


Figure (1.3): High resolution Transmission electron microscope (HRTEM) image of 40nm diameter Bi nanowires[36]

Jim etal. in 2004 formed electrically conducting mesoscale and nanoscale Bi and Sb wires through self assembly of atomic clusters using an inert gas aggregation source to form clusters assembled wires on unpassivated, and SiO_2 passivated, V- grooved Si substrates. V- grooves (4-7µm in width, 6µm-1mm in length) were prepared using optical lithography and anisotropic etching in KOH solution. The effectiveness of the surface templating technique was demonstrated by scanning electron microscope analysis carried out after deposition from Bi cluster wires. It is clear the correlation between the width of the cluster free area and the source argon low. When argon flows exceed ~150 ccm, the walls of 4-7μm wide SiO_2, V-grooves typically have zero cluster occupancy and there is a well defined cluster assembled wire at the apex of the grove . Sb cluster assembled wire have linear I-V characteristic taken from this wire and the resistance is ~0.7MΩ which is less than Bi cluster wires. This resistance is considerably higher than the value expected from the bulk resistivity values of Sb wires. The main cause for this high resistance is thought to be the granular nature of the wire and to some degree oxidation of the cluster[36].

Huber etal. and Gwart in 2005 prepared high density network of 6nm diameter Bi wires by melting pure Bi (99.9999%) and injecting it into porous Vycor glass (PVG) by applying a hydrostatic pressures of 5 kbar . The PVG used has an average pore diameter of 6nm. The inter connected network of pores occupies about 30% of the volume X-ray diffraction from the Bi- PVG composite shows the Bi retins its rhomboheral structure but with shrinkage of its unit cell. An estimate for the average Bi crystalline size (D) can be obtained from the widths of the (XRD) peaks through Scherres equation. The Bi quantum wires composite was exposed by etching with HF and the electron scanning micrograph image showed these samples are not very stable. The resistance (R) of high density network of 6nm diameter, Bi wires increases from 300 K to below 4 K, where R varies about as in (1/T). The order of magnitude of the resistance arise, as well as the behavior of the magneto resistance are consistent with localization and electrons – electron interaction[37] .

Rong etal. in 2005 fabricated bismuth nanowires by electrochemically depositing Bi into porous polycarbonate (PC) membranes at room temperature. One of the advantages of this technique is that the more morphology of the fabricated nanowires can be controlled, to a large extend by selecting appropriate additives , PH, deposition potential and temperature. The Bi electrolyte was prepared by certain procedure. The observation of superconductivity in granular Bi nanowires fabricated by electrochemical deposition at room temperature and measured at ambient pressure show that the Bi nanowires can be superconducting or non- superconducting sensitively depending on the details of sample morphology . Bismuth nanowires (granular of rhombohedral grains of ~ 10 nm diameter) have two transition temperature, T_c of 7.2 and 8.3 K . These T_c values concide with T_c values of the high pressure phases Bi- III and Bi- V , respectively as shown in figure (1.4). The analysis arise, from this study that structural analysis and transport data indicate that superconductivity of granular Bi nanowires probably arises from grain boundary areas where there are structural reconstructions between the grains showing a preferred orientation within a small angular distribution[38].

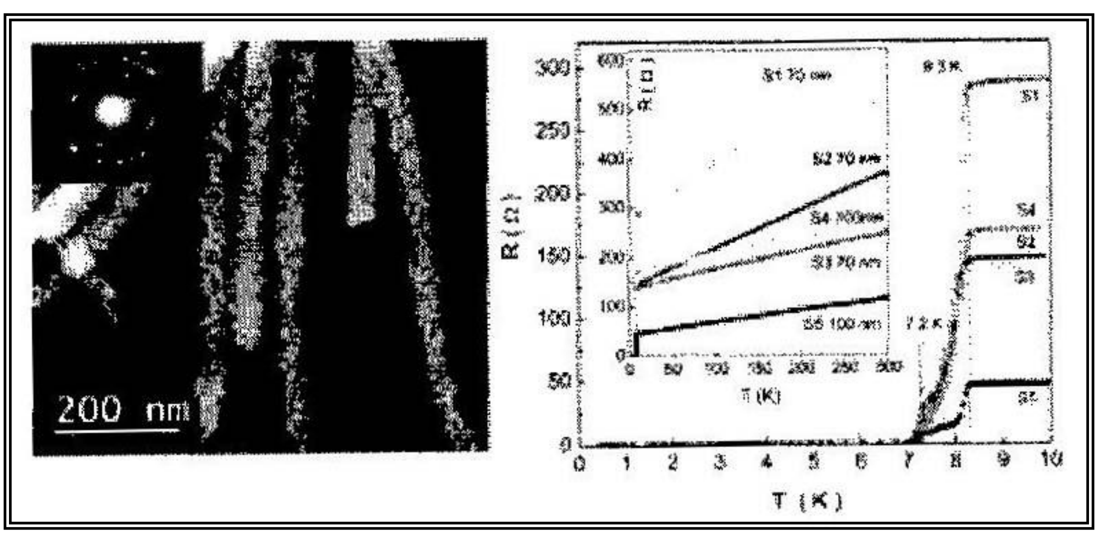


Figure (1.4): Granular bismuth nanowires and their critical temperature[42]

Cornelius in 2006 investigated single bismuth nanowires by means of infrared (IR) and electron energy loss spectroscopy (EELS). Arrays of Bi wires were deposited electrochemically in etched ion- trach membranes. The IR spectra show an absorption on set shifting to higher energies for smaller wire diameter. Measurement using linearly polarized light showed that there are at least two transitions . The transition excited by light whose electric wave vector oscillates normal to the wire axis, exhibits a stronger energy shift than that induced by a parallel polarized light. T.W. Cornelius ascribe them to direct transitions in the vicinity of the L- point and indirect transitions from the L- to T point valance band respectively[39].

Partridge etal. in 2007 prepared bismuth clusters with an average diameter of 25 nm such clusters have been deposited in an inert gas aggregation source like in their work in 2004[32]. Bi cluster was assembled into thin – film interconnects which are formed between planer electrical contacts and supported on Si substrates passivated with Si_3N_4 or thermally grown oxide. A layer of SU8 (a negative photo resist based on

Epon SU-8 epoxy resin) is patterned using optical or electron- beam lithography, and it defines the position and dimensions of the cluster film. The conduction between the contact is monitored throughout the depositional assembly process and subsequent I-V characterization is performed in situ. Bi cluster assembled interconnets have been fabricated with nanoscale widths with and with up to 1:1 thinkness : width aspect ratios. The conductivity of these interconnects has been increased , post deposition, using a simple thermal annealing process. The wires consist of nanopaticles separated by tunnel junctions result non linear I-V characteristics and temperature dependent. Further more it is difficult to control the conductivity of the assembled wires and films during fabrication means that sample to – sample consistency is hard to achieve. The resistance for single cluster assembled wire was 71kΩ, which corresponds to resistivity approximately many times in comparison to the bulk . The granular nature of the wire and some of the oxidation causes this high resistance. At V=7V and I=105µA , this wire irreversibly ceased to contact the maximum current density in this wire (1µm width 100 µm length and 50nm thickness) was estimated to be approximately 10^6 Acm^{-2} . Figure (1.5) shows I-V characteristics of Bi cluster assembled obtained and the resistance was 10kΩ. A heater and temperature controller were used to raise the temperature of the sample to 300,330,370,400,430 and finally 460K. The resistance interconnect was decreased as the temperature of the sample increased[40].

The resistance at 460K was 5.8kΩ . They were then cooled to room temperature and find resistance of 6.5kΩ was measured (30% lower than the as – deposited resistance and corresponding to resistivity approximately five times that of the bulk). The increase in conductance of the wire after annealing is due to the increased coalescence of the Bi clusters at elevated temperatures and a permanent change in the morphology and grain size of the wire[33]. The resistance of the wire was decreases with increasing temperature[40].

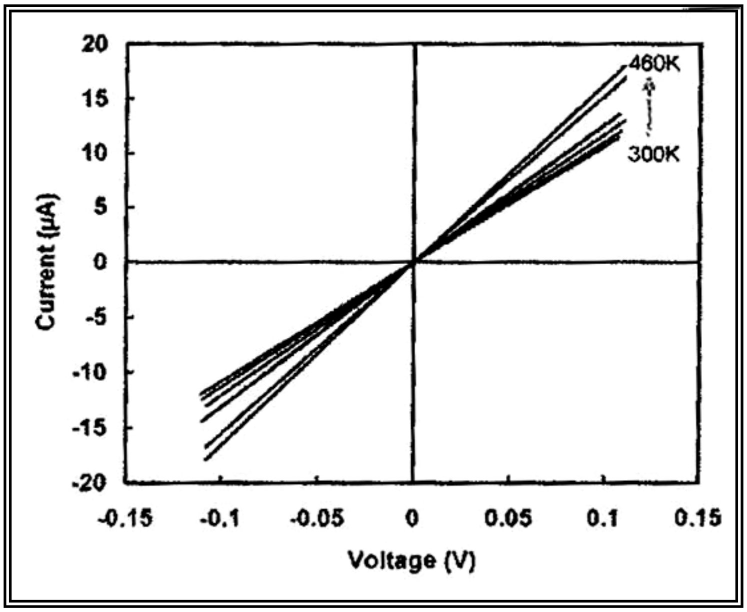


Figure (1.5): The I-V characteristics of a Bi cluster- assembled interconnect length 100μm and minimum width 1μm at 300-460K[44].

The progress in understanding the physical phenomenon of superconductivity and the appearance of other kinds with different applications depend on the advancement in materials research that is still in progress. With Onnes discovery, many scientists and researchers were interested in studying the phenomena itself or to produce other materials having higher T_c and approaching to produce new compounds having zero resistance approach or to clarify the mechanism of high T_c superconductivity.

Chapter 2

2-1 Introduction

Making a case of room temperature superconductivity is the great challenge of many researchers in the word and a holy grail of solid state physics since 1982 till this day. Several surprises are begun to emerge from studies of bismuth nanostructure. Starting with Bourgoin filaments (1982 and 2005)[16] Huber and[37] Dersselhaus[31] and others who worked experimentally and theoretically on bismuth nanowires (2007). They produced a great experience in electrical transport in bismuth nanowires. The two fluid model , percolation theory and proximaty effect are ideas that depend on the understanding and explanation of the high conductivity of bismuth filament and it will be shown in this chapter in addition to the items which are useful to overcome in this study.

2-2 Conductive Composite (metal / insulator)

Manufacturing processes usually involve three basic steps to get composite compound, and as follows[41]:-

i) Combination of the matrix material with the filler.

ii) Alignment of the filler into a specific configuration or pattern using magnetic , electrostatic, vibratory, rolling or flotation techniques.

iii) Consolidation of the combined constituents. This is normally obtained by compression and/or heat treatment.

The most common advanced composite is polymer matrix composite (PMC). The composite consists of a polymer, e.g. epoxy resin, polyester and urethane with other material (metal, ceramic, or fiber glass). The reason why they are the most common composite includes their low cost, highly strength , and simple manufacturing principles[41].

2-3 Electrophoresis

It is an industrial process in which collided particles in a liquid insulator medium migrate under the influence of an electric field. It provides a good means of applying matrix material (suspension solid state matrix process or molten particle to continue filaments without the use of high temperature. These produce a composite with multifilament with very little degradation of fiber (filament) properties as compared to other methods. This electrochemical technique, that formed composite show higher mechanical properties than those produced by powder metallurgy[42].

The charge of the colloidal particles plays an important role in the electrophoretic mobility. The surface tension of the particles , electrical resistance of the insulator matrix and the electrodes are dependent factors on the rate of electroforming pin process. It also varies greatly with strength of the applied field. What insures high rate of forming rate is also inducing porosity in the filament formation[43].

Composite materials are able to provide benefits over both metal and unreinforced plastic. In order to increase the future use of plastic composites with high electrical conductivity (ultra conductor or room temperature superconductors) in engineering application , novel polymers (high resistance temperature) and fillers (high purity and very fine superconductor metal powder) will be required. Aerospace and computer technology or nanotechnology applications need such conductive composite materials (filaments) in a very wide range[44].

2-4 Electrophoretic Migration

When a particle of electrical charge q is subjected to electrical field strength (potential difference), a force of magnitude (qE) results. This construction force causes acceleration of the particle until the accelerative forces balanced by the frictional resistance (f_r) exerted by the medium in which the particle moves. The particle attains a constant velocity of migration (electrophoretic), a velocity (v) which reflects the difference between the two opposite forces. The equilibrium conditions can be most generally expressed by[45].

$$qE = f_r = \frac{KT}{d}\upsilon \quad .... \quad (2-1)$$

where d is the diffusion constant of the particle under given conditions , K the Boltzman constant , and T the absolute temperature in Kelvin (K).

In free solution and spherical particles , f_r obeys Stokes law.

$$f_r = \sigma \pi r \upsilon \eta \quad .... \quad (2-2)$$

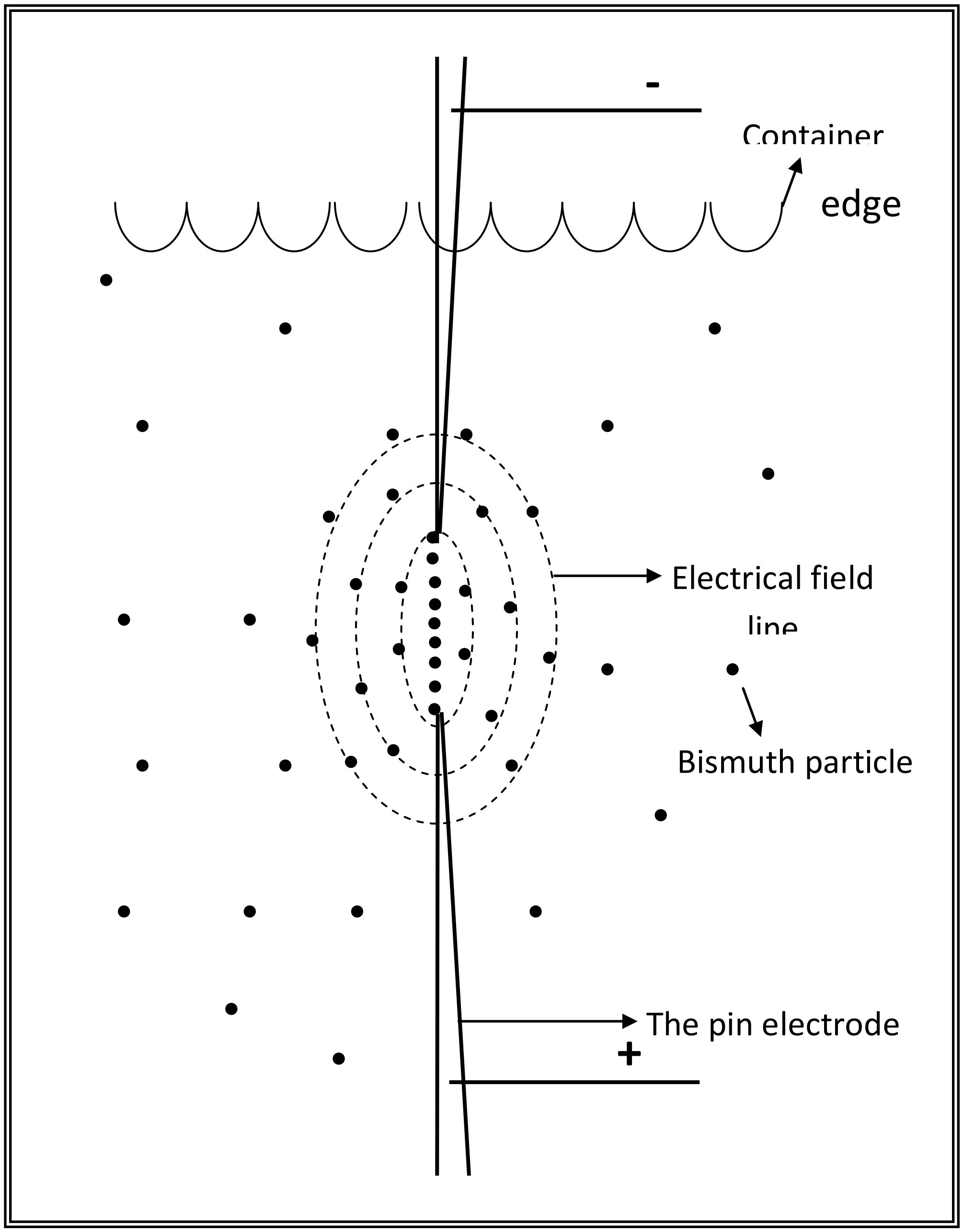
where r is the particle radius and η the medium viscosity. As q is the number Z of unit charges e and E is the ratio of current density J to the specific conductivity (ohm.cm)$^{-1}$ (σ), then υ can be expressed as[40]:-

$$\upsilon = \frac{qEd}{KT} = \frac{ZeJd}{KT\sigma} \quad .... \quad (2-3)$$

The velocity attained by a charged particle in an electric field of unit strength (V/cm) is defined as the mobility (m) measured in cm^2 /(V.sec). It is the measured migration distance x of the particle under unit conditions of time t and E will be[46] :-

$$m = \frac{\upsilon}{E} = \frac{x}{tE} = \frac{q}{f_r} = \frac{Zed}{KT} \quad .... \quad (2-4)$$

Under given electrophorcetic conditions, m is a physical constant proportional to x. Only under identical conditions of t and E, the values of x can be compared directly. Figure (2.1) shows the mechanism of electrical migration of conductor particles between two pin electrodes having oppositely applied voltage[16].


-
Container
edge
Electrical field
line
Bismuth particle
The pin electrode
+

dc voltage

Figure (2.1) : Migration of conductor Bi particles between electrical pins[16]

2-5 Bi Semimetal Solidification Process

The change in a metal or semi-metal powder from a solid state to a liquid state condition is achieved by the increased vibration activity of the atomic structure as the temperature of the metal increases. The vibration becomes vigorous enough to break bonds, the atoms loss their ordered geometric positions and start moving at high velocities in all directions. Mixing or stirrring make this process faster and get finer particles with less time. The metal is now in a semi-liquid state than to liquid state and still exist very weak forces of attraction between the atoms. When the temperature of molten metal starts of fall velocity of the moving atoms begin to decrease , i.e. the kinetic energy of the atoms decreases. As the random motion of atoms becomes slow due to heat loss; contact between some atoms will occur. These contacts will result in the formation of nuclei around which metal crystals will eventually form. The growth of the crystal will render the liquid where viscous and solidification can be considered to start. During the solidification process; the atomic formation is developed and grows in particular, an ordered arrangement but in random directions[47]. The ordered patterns are characteristic of a particular metal. Figure (2.2) shows the thermal equilibrium curve of bismuth semi metal[47]

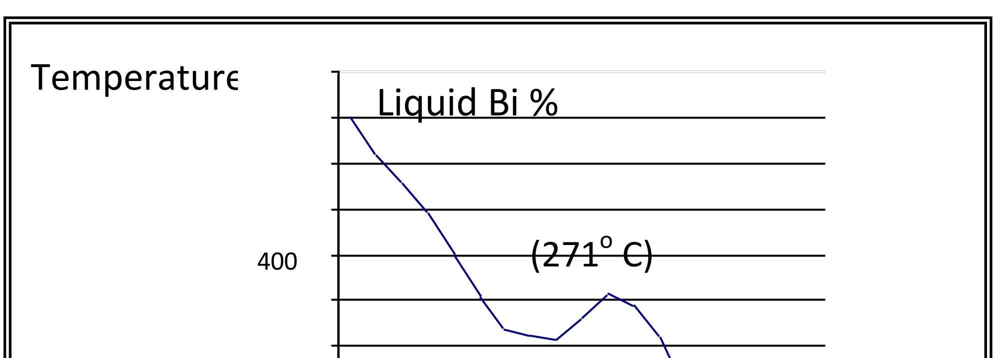


Figure (2.2): The cooling curve for pure Bi semimetal[47]

2-6 Two Fluid Model

Long before the (BCS) theory was established, a two fluid model was used as an attempt to formulate a two- fluid theory to explain the known properties of superconductivity. This model assumes that the electron fluid in a superconductor can be imagined as a mixture of superconducting and normal electrons. The properties of normal component are identical to all electrons without any difference between free or bound electrons . While the superconducting components which are responsible for the anomalous properties are identical to superelectrons. These electrons exhibit no scattering with decreasing temperature; that means the superconducting fraction grows while the density of the normal component decreases and finally vanishes at zero temperature[3]. The reason to treat conduction electrons flow as a fluid flow; is considering the partical density within the range of particle densities in fluid media and all fluids exhibit viscosity or internal friction (resistance), just as a coefficient of viscosity (fluid resistivity). The superelectrons (pairs) can pass along the conductor with velocities in excess of thermal agitation velocity tending to disrupt their flow. It has been postulated that the fast electron component has a flow velocity of the order of 10^7 cm/sec[3,48].

Bourgion and Carrol in 1982 suggested an explication for a high conductivity of bismuth filament of (1-4)mm length that the desired electron pairing could be affected if the electrons were forced , into proximity upon entry and extremely narrow conductor; conductor would have to be a material where electron flow velocities under normal conditions of conduction were quite high. If, extermaly, the narrow conductor would be created of such a material, the thermal agitation velocity and ambient temperatures would have little effect on the electron pairs. Carrol and Bourgion expected that the forced proximity would cause the electrons to pair in an orientation of least potential , i.e. with spin annulling[16,28].

2-7 Raw Materials

2-7-1 Bismuth Properties

The material selected for thin conductor was bismuth since it is semimetal known to contribute only one conduction electron per 10^5 to 10^6 atoms. The atomic density of Bi is 2.82×10^{22} atom/cm^3 [48]. The conduction electron density in Bi is 5.65×10^{16} conduction electron /cm^3 [43].Bourgoin and Carrlo found that the main reason of high resistance of metals is due to the collisions of electrons in a current flow with the vibrating lattice. They calculated the velocity of electrons from Boltzman form equating mechanical energy to thermal energy[48].

$$\frac{1}{2}Mv^2 = KT \quad .... \quad (2-5)$$

where

M: is the mass of particle in the lattice structure in grams.

v : is the velocity in cm/ sec.

K : Boltzman constant (1.38×10^{-16} erg/ K).

T : absolute temperature in K.

A lattice electron of mass M_e= 9.11×10^{-28} at room temperature (27 ^oC or 300K) will vibrate at a rate of velocity[16] :-

$$v = \sqrt{\frac{2KT}{M_e}} = 0.95 \times 10^7 \, cm/\sec \quad .... \quad (2-6)$$

This is high speed and close to electron pair (super electrons) order velocity and this is referred to as the thermal agitation velocity. The current flow velocity or the drift velocity is found by the use of current equation [48] :-

$$I = A.N.e.v \quad ....(2-7)$$

where

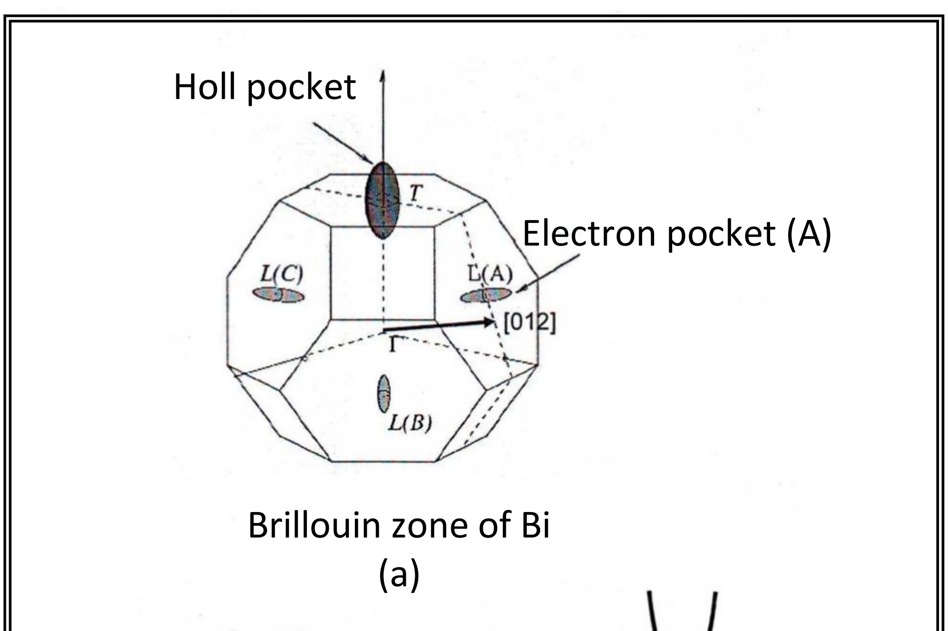
I:- magnitude of current in Amperes .

N:- conduction election density in electron /cm^3 .

A:- conductor cross section in cm^3.

e:- charge of electron (1.6×10^{-19} Coulomb/electron)[47] .

Bismuth (Bi) is a very attractive material for the study of low dimensional systems. Bismuth as shown in Table (2-1)[50] is a group V semimetal in which the electrons are distributed in three highly isotropic carrier pockets at the L-point of the Brillowin zone and the holl pockets are contained in one a pocket at the T- point of the Brillion zone as it shown in figure (2.3)[51].



Brillouin zone of Bi
(a)

Figure (2.3): (a): Bismuth crystalline structure

(b): Energy band splitting with smaller diameters of bismuth nanowires[51]

Table (2-1): Bismuth Semimetal Properties[50]

General

Name, Symbol, Number	Bismuth, Bi, 83
Chemical series	Poor matals
Group, Period, Block	15, 6, p
Appearance	Lustrous reddish white
Atomic mass	208.98040(1) g/mol
Electron configuration	[X] $4f^{14}$ $5d^{10}$ $6s^{2}$ $6p^{3}$
Electrons per shell	2, 8, 18, 32, 18, 5
Physical properties	
Density (near r.t.)	9.78 g/cm^{3}
Liquid density at m.p.	10.05 g/cm^{3}
Melting point	544.7K (271.5 ^{o}C, 520.7 ^{o}F)
Boiling point	1837 K (1564 ^{o}C, 2847 ^{o}F)
Heat of fusion	11.30 kJ/mol
Heat of vaporization	151 kJ/mol
Heat capacity	(25 ^{o}C) 25.52/(mol-K)
Vapor pressure	

P/Pa	1	10	100	1k	10k	100k

at T/K	941	1041	1165	1325	1538	1935

Atomic properties	
Crystal structure	rhombohedral
Oxidation states	3, 5 (mildly acidic oxide)
Electronegativity	2.02 (Pauling scale)
Ionization energies (more)	1^{st} : 703 kJ/mol
	2^{nd} : 1610 kJ/mol
	3^{rd} : 2466 kJ/mol
Atomic radius	160 pm
Atomic radius (calc.)	143 pm
Covalent radius	146 pm
Miscellaneous	
Magnetic ordering	Diamagnetic
Electrical resistivity	(20 ^{o}C) 1.29 µ Ω.m
Thermal conductivity	(300 K) 7.97 W/(m-K)
Thermal expansion	(25 ^{o}C) 13.4 µm / (m-K)
Speed of sound (thin rod)	(20 ^{o}C) 1790 m/s
Young's modulus	32 GPa

Shear modulus	12 GPa
Bulk modulus	31 GPa
Poisson ratio	0.33
Mohs hardness	2.25
Brinell hardness	94.2 MPa
CAS registry number	7440-69-9
Notable isotopes	
Main article : Isotopes of bismuth	

Iso	NA	half-life	DM	DE (MeV)	DP
^{207}Bi	syn	31.55y	ε, $β^+$	2.399	^{207}Pb
^{208}Bi	syn	3,368,000y	ε, $β^+$	2.880	^{208}Pb
^{209}Bi	100%	$(1.9±0.2)×10^{19}$y	α		^{205}Tl

The small energy overlap (38 meV at 77K) in bulk Bi between the L-point conduction band and T-point valance band is predicted to vanish in Bi nanowires when the diameter is smaller than; 50 nm thus causing a semimetal – to semiconductor transition due to quantum confinement effects[45]. Figure (2.4) shows the structure of energy band gap of semimetal Bi[52].

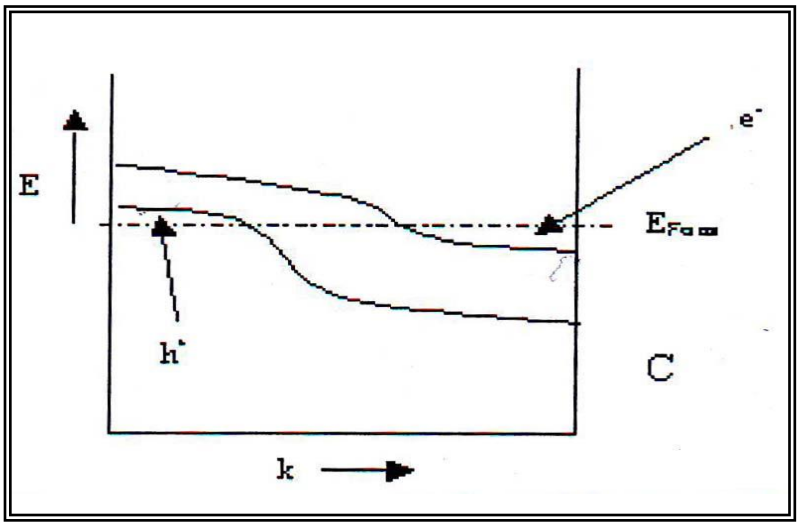


Figure (2.4):- Semimetal Bi energy band diagram[53]

Bismuth has a highly un isotopic Fermi surface that made it of more variability for band structures. Conduction electron in bismuth bulk has long free mean path λ ~ 0.4 nm at 4 K and that makes it suitable for studying transport properties[54]. In addition bismuth has a low carrier concentration (~ 10^{18} electron /cm^3) which makes it easily managed by doping i.e. Te (n-type) or Pb, Sn (p-type)[55].

2-7-2 Epoxy Resin

Epoxy resin is one of major industrial plastics . When converted by curing agent (hardener) , the thermosetting resins become a hard infusible system . The system may be visualized as net work cross – linked in all three dimensions .Epoxy resin are characterized by the oxiran rings[56]. The most widely used resins are based on the reaction of bisphenol A and epichlorohydrin cured with amines as shown as follows by the chemical reaction[56].

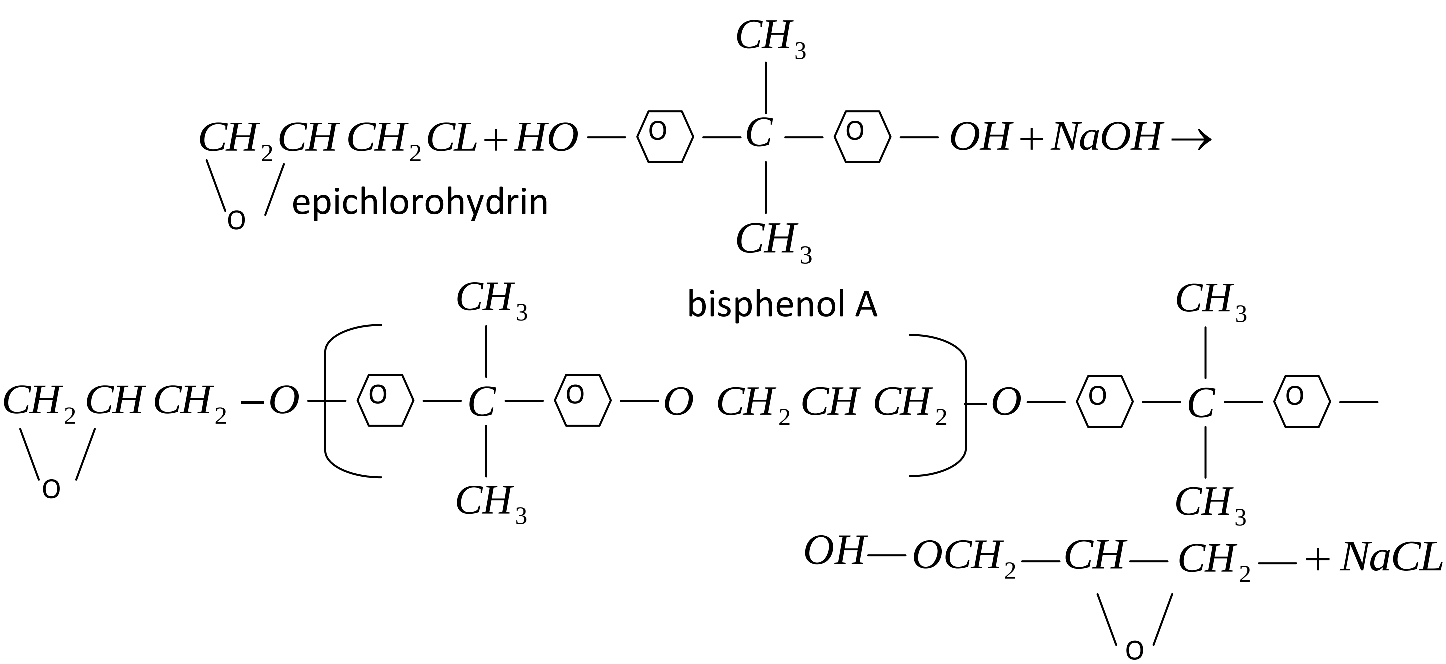
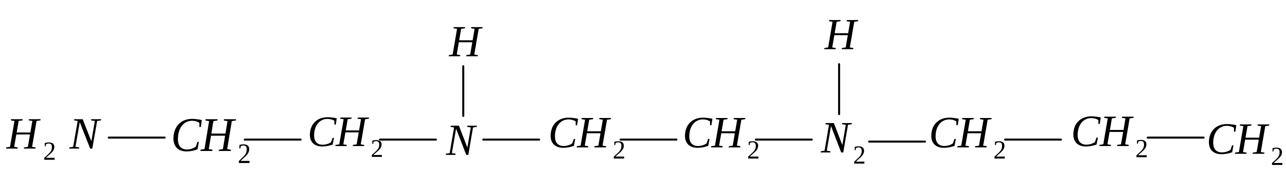


Figure (2.5):- Epoxy chemical reaction[57]

Epoxies react by curing opening mechanism. It is necessary to have a catalyst and a hydrogen donor (such as H_2O or hydrogen group). Usually, primary, secondary or tertiary amines will act as a catalyst and hydrogen donor[57].

Triethylene tetramine (TETA) is the hardener used in this study which has the following structure[58]:-



Epoxies take the following form reaction when react with tertiary amines[57].

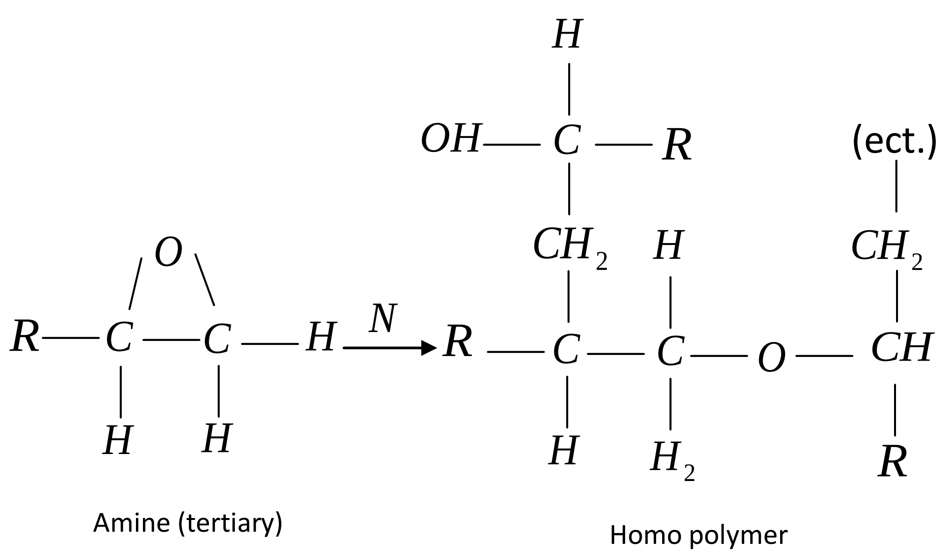


Figure (2.6): Curing mechanism of epoxy resin and the catalyst triethylenetetramine (TETA)[57]

2-8 Percolation Phenomena Moldelling of Random Medium

Percolation theory is a method for disordered medium (metal/insulator) and a critical phenomenon where at a critical value the system will obey to sudden changes. This phenomenon is used to explain many physical and chemical effects. Such a system consists of composite mixture of conductor and insulator components. Percolation theory is suitable to explain the electrical conductivity in polymer. Conductor composite material (CCM) which discusses the connection probability (P) between a large number of conductor particles randomly disperses within the polymer, each particle contacts with the neighbours of other random particles. As much the particles are close to each other for distance so as the charge carriers transition probability is more than zero. When the metal (conductor) concentration reach “Threshold percolation” which is the least concentrations for the metal particles used to form conducting network having many current paths that allowed for charge carriers movement and percolated through the network[59,62]. Figure (2.7) shows percolation phenomena in example lattice of metal and insulator particles[59] having percolation phenomena.

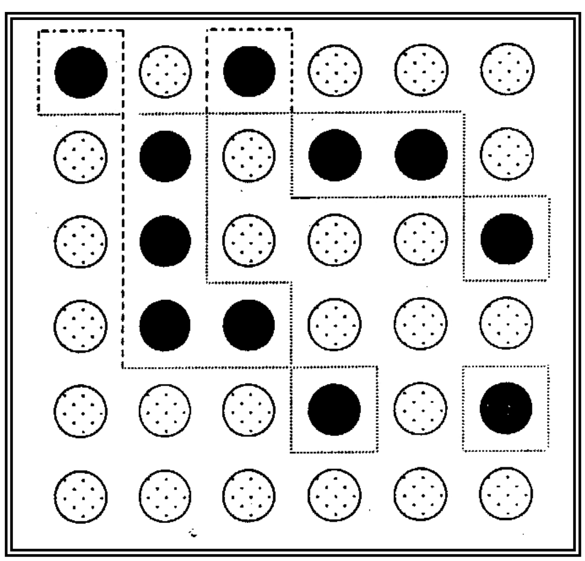


Figure (2.7) An example lattice of metal particle

● Metal partical ○ polymer partical[59]

2-9 Interaction of Gamma Rays With Matter

Gamma radiation is electromagnetic radiation of wavelength below (0.1-10) nm produced from atomic nucleus. The main interactions of γ-rays with matter are[60] :-

1) Photoelectric effects.

2) Compton scattering including (Thomson and Raleigh scatterings).

3) Pair production.

These reactions explain the two principal qualitative feature of X- ray and γ- rays :-

First; X-rays and γ- rays are many times more penetrating in matter than charged particles (α , β or P) and second a beam of photons is not degraded in energy as it passes through a thickness of matter, only attenuated in intensity[64].

The first feature is due to the much smaller cross sections of the three processes relative to the inelastic electron collision cross section. The second characteristic , however,is due to the fact the three processes above remove the photon from the beam entirely, either by absorption or scattering. The total number of photons reduced by the number interacted with the a target materials.

The attenuation suffered by a photon beam can be exponential with respert to the thickness of the target i.e.[61]:-

$$I(x) = I_0 \exp(-\mu x) \quad \text{..........} \quad (2-8)$$

where I_o is the intial inciden beam intensity (photon /cm^2); (x) is the thickness of absorber (cm^2), μ is the absorber coefficient in (cm^2/gm) which depends on the chemical composition of the specimen and the energy of gamma- rays photon. The total probability for a photon interaction in matter is the sum of the individual cross sections of the above outlined processes.

2-10 Radiation Effect

Certain type of radiation (electron beams, X-Rays, β and γ-rays, and ultraviolet radiation) possess sufficient energy to pentrate a material (polymers or metal) and interact with the constituent atoms or their electrons. One such reaction is ionization in which the radiation removes an orbital electron from specific atom, converting that atom into positively charged ion. As a consequence , one of the covalent bounds associated with the specific atom at that point. This bound breaking leads to either scission or cross- linking at the ionization site depending on the chemical structure and on the dose of radiation.

Phase Transformation defined as structural change which required an energy to be exhibited. Two kinds of transformation could be occurred related to gamma irradiation for phase transformation in metals. First kind called displacive transformation in which the bonds are distortion without broken so the change in the structure is usually small that required small activation energy. The second kind called reconstructive transformation in which complete change take place in the structure because most at the bonds may broken and new bonds will be formed so it requires high activation energy [62].

2-11 The Aim of The Study

The present study is undertaken to prepare bismuth filaments within insulator matrix as (metal / polymer) composite hoping to have high conductive Bi filaments by the guide lines of Bourgoin experiments.

The objectives of the study include :-

1- Examining the physical properties of the raw materials by using x-ray diffraction , x-ray fluorescence, FTIR , DSC analysis , grain size distribution (LDPSA) and optical microscopy(OM) examinations.

2- Determining the controlling parameters of forming bismuth filament using electrophorieses migration technique starting with:-

i) The suitable values of the applied DC. voltage by which Bi powder particles affected to forme a filament.

ii) The determination of suitable electrodes and molds materials in the preparation process.

iii) Selection of better process conditions to get bismuth filament at room temperature and at Bi melting point temperature.

3- I-V characterization of Bi filaments prepared by cold work (room temperature) and hot work (271 and at 310) ^{o}C using 2- probe resistance measurements.

4- Examining the gamma irradiation effect on the electrical I-V characterization of the prepared filament.