BAND GAP AND RESISTIVITY MEASUREMENTS OF SEMICONDUCTOR MATERIALS FOR THIN FILMS

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ABSTRACT: *This article briefly reviews and explores the basic properties of semiconducting materials, band gap, resistivity measurements and its applications in electronics and solar cells. The semiconductors are solid crystalline substances that tend to have greater electrical conductivity than insulators, but less than good conductors. The valence band of a semiconductor is full similarly to that of an insulator, but the band gap is much smaller (about 1 eV compared to about 5eV). In fact, the band gap in several semiconductors is so small that electrons are easily able to be thermally excited into the conduction band. This means that the electrical conductivity of many semiconductors is strongly reliant on temperature. Even though conductivity is not dependent only on the number of free electrons, materials with less than one free electron per million atoms will not easily be able to conduct electricity. To have practical uses for semiconductors the conductivity must be greatly increased and raising the temperature is not a very reliable way to achieve this goal. However, it is accomplished by doping (adding a very small amount of other atoms in with the semiconductors).*

Keywords: Semiconductor Material, Si and Ge, Conductivity, Resistivity, Band Gap, Doping, etc.

I. INTRODUCTION

The semiconductor materials and devices have been of great interest throughout the history of semiconductor technology world. As the name suggests, semiconductor is a material which cannot conduct completely, instead its conduction ability lies between that of an insulator and a conductor. This means that they have a resistivity too low to be called an insulator but at the same time, too high to be called a conductor. Devices made from semiconductor materials are the foundation of modern electronics, including ratio, computers, telephones, and may other devices. Semiconductor devices include the transistor, many kinds of diodes including the light emitting diode, the silicon controlled rectifier, and digital and analog integrated circuits. Solar photovoltaic panels are large semiconductor devices that directly convert light energy into electrical energy. In a metallic conductor, current is carried by the flow of electrons. In semiconductors, current can be carried either by the flow of electrons or by the flow of positively charged holes in the electron structure of the material. So many other materials are used, including germanium, gallium arsenide. The best-known semiconductor is undoubtedly silicon (Si). However, there are many semiconductors besides silicon. Semiconductors constitute a large class of substances which have resistivity lying between those of insulators and conductors. The resistivity of semiconductors varies in wide limits from 10^{-4} to 10^{4} Ω-m and is reduced to a very great extent with an increase in temperature. The most typical and extensively employed semiconductors, whose electrical properties have been well investigated, are Germanium (Ge), Silicon (Si) and Tellurium (Te). The study of their electrical properties reveals that semiconductors have *negative temperature Coefficient of resistance*, *i.e.*, the resistance of semiconductor decreases with increase in temperature and vice versa.

II. SEMICONDUCTOR MATERIALS

The best-known semiconductor is undoubtedly silicon (Si). Silicon is used to create most semiconductors commercially. However, there are many semiconductors besides silicon. PV cells are made of semiconductor materials. The semiconductors are solid crystalline substances that have properties of greater electrical conductivity than insulators, but less than good conductors. A semiconductor material is one whose electrical properties lie in between those of insulators and good conductors. The electrical conductivity of a semiconductor is very much affected when a suitable impurity, *e.g.*, Arsenic, Gallium, Indium etc. is added to it. The major types of semiconductor

materials are crystalline and thin films, which vary from each other in terms of light absorption efficiency, energy conversion efficiency, manufacturing technology and cost of production. This property of semiconductors is most important for PV solar cells. The valence band of a semiconductor is full similarly to that of an insulator, but the band gap is much smaller (about 1eV compared to about 5eV). In terms of energy bands, semiconductors can be defined as those materials which have almost an empty conduction band and almost filled valence band with a very narrow energy gap (of the order of 1eV) separating the two. The conductivity of a semiconductor material can be varied under an external electric field. The resistivity of semiconductors lies between that of a good insulator and of a metal conductor lying in the range 10^{-4} to 10^{4} Ω-m. The defining property of a semiconductor material is that it can be doped with impurities that alter its electronic properties in a controllable way. Semiconductor materials are differing by their properties. Compound semiconductors have advantages and disadvantages in comparison with silicon. For example gallium arsenide has six times higher electron mobility than silicon, which allows faster operation; wider band gap, which allows operation of power devices at higher temperatures, and gives lower thermal noise to low power devices at room temperature; its direct band gap gives it more favorable optoelectronic properties than the indirect band gap of silicon; it can be alloyed to ternary and quaternary compositions, with adjustable band gap width, allowing light emission at chosen wavelengths, and allowing e.g. matching to wavelengths with lowest losses in optical fibers. GaAs can be also grown in a semi insulating form, which is suitable as a lattice-matching insulating substrate for GaAs devices. The semiconductor materials and its impurities is shown in table (1). The Energy Bands in Insulators, Semiconductors, and Conductors is shown in fig. (1).

Table (1): semiconductor materials and its impurities.

Acceptor Impurities	Semiconductor	Donor Impurities
Group III (p-type)	**Group IV**	**Group V (n-type)**
Boron 5	Carbon 6	Nitrogen 7
Aluminum 13	**Silicon 14**	**Phosphorus 15**
Gallium 31	Germanium 32	**Arsenic 33**
Indium 49	Tin 50	**Antimony 51**

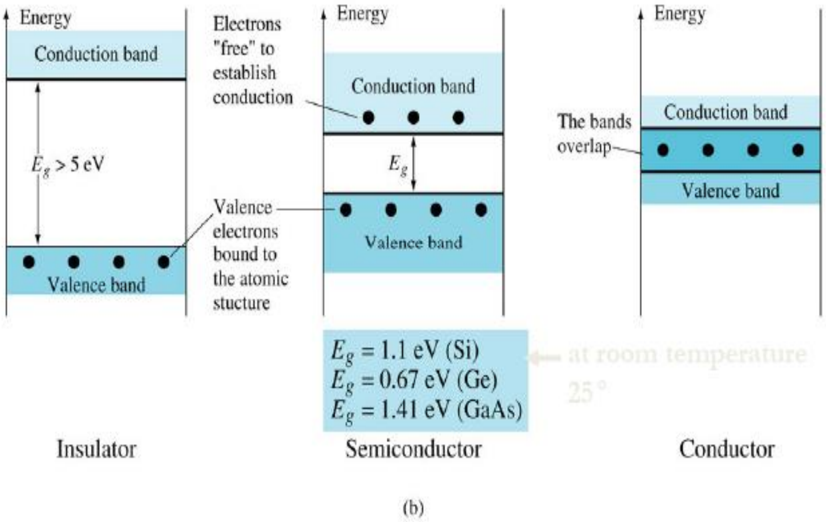


Fig. (1): Energy Bands in Insulators, Semiconductors, and Conductors

III. TYPES OF SEMICONDUCTORS

There are two types of Semiconductors:

(1) INTRINSIC OR PURE SEMICONDUCTORS: An intrinsic semiconductor is one which is made of the semiconductor material in its extremely pure form. Examples of such semiconductors are: pure germanium and silicon which have forbidden energy gaps of 0.72 eV and 1.1 eV, respectively. The energy gap is so small that even at ordinary room temperature; there are many electrons which possess sufficient energy to jump across the small energy gap between the valence and the conduction bands. Alternatively, an intrinsic semiconductor may be defined as one in which the number of conduction electrons is equal to the number of holes.

(2) EXTRINSIC OR IMPURE SEMICONDUCTORS: When some suitable impurity or doping agent or doping is added in extremely small amounts (about 1 part in 10^8) in pure semiconductor materials are called extrinsic or impurity semiconductors. After the adding of some impurities their resistance and electrical properties change and they are known as extrinsic semiconductors. An impurity is introduced into a semiconductor (*doping*) to change its electronic properties. The N-type have impurities with one more valence electron than the semiconductor. The p-type has impurities with one fewer valence electron than the semiconductor. Those intrinsic semiconductors to which some suitable impurity or doping agent or doping has been added in extremely small amounts (about 1 part in 10^8) are called extrinsic or impurity semiconductors. Depending on the type of doping material used, extrinsic semiconductors can be sub-divided into two classes:

[i] **N-TYPE:** The silicon doped with extra electrons is called an "N type" semiconductor. The "N" is for negative, which is the charge of an electron.

[ii] **P-TYPE:** Silicon doped with material missing electrons that produce locations called holes is called "P type" semiconductor. The "P" is for positive, which is the charge of a hole.

[a] GROUP IV ELEMENTAL SEMICONDUCTORS

Diamond (C) (5.47 eV)
Silicon (Si) (1.11 eV, indirect band gap, most common semiconductor, easy to fabricate)
Germanium (Ge) (0.67 eV, indirect band gap)

[b] GROUP IV COMPOUND SEMICONDUCTORS

Silicon carbide (SiC)
3C-SiC (2.3 eV)
4H-SiC (3.3 eV)
6H-SiC (3.0 eV)
Silicon-germanium (SiGe) (0.67-1.11 eV)

[c] Group III-V SEMIONDUTORS

Crystallizing with high degree of stoichiometry, most can be obtained as both n-type and p-type. Many have high carrier nobilities and direct energy gaps, making them useful for optoelectronics.

Aluminium antimonide (AlSb) (1.6 eV)
Aluminium arsenide (AlAs) (2.16 eV, indirect band gap)
Aluminium nitride (AlN) (6.28 eV, direct band gap)
Aluminium phosphide (AlP) (2.45 eV)
Boron arsenide (BAs) (1.5 eV, indirect band gap)
Gallium antimonide (GaSb) (0.7 eV)
Gallium arsenide (GaAs) (1.43 eV, direct band gap, second most common in use, commonly used as substrate)
Gallium nitride (GaN) (3.44 eV, direct band gap)
Gallium phosphide (GaP) (2.26 eV, indirect band gap)
Indium antimonide (InSb) (0.17 eV, direct band gap)
Indium arsenide (InAs) (0.36 eV, direct band gap)
Indium nitride (InN) (0.7 eV)
Indium phosphide (InP) (1.35 eV, direct band gap, commonly used as substrate)

[d] GROUP II-VI SEMICONDUCTORS

Cadmium selenide (CdSe) (1.74 eV, direct band gap)
Cadmium sulfide (CdS) (2.42 eV, direct band gap, common for quantum dots)
Cadmium telluride (CdTe) (1.49 eV)
Zinc oxide (ZnO) (3.37 eV, direct band gap)
Zinc selenide (ZnSe) (2.7 eV)
Zinc sulfide (ZnS) (3.68 eV)
Zinc telluride (ZnTe) (2.25 eV)

IV. BAND GAP (Eg) SEMICONDUCTOR MATERIALS

The history of semiconductors is presented beginning with the first documented observation of a semiconductor effect (Faraday), through the development of the first devices and the theory of semiconductors up to the contemporary devices. The semiconductor used needs to have a low enough energy band gap to absorb the solar spectrum effectively and to control the electrical processes involved in energy conversion. Given this, it is very clear that the material used in the photovoltaic cells play a major role in its functioning. Recent research has also investigated the use of multi-junction cells in which two (or more) different cells are used together, to produce the energy more efficiently. One of the landmarks of 1988 was the achievement of a 31% efficient solar cell with a combination of a single-crystal GaAs (with efficiency of 27.2% when used alone) along with a back-contact single-crystal Si (with efficiency of 26% when used alone). The measurement of the band gap of materials is important in the semiconductor, nanomaterial and solar industries. The term "band gap" refers to the energy difference between the top of the valence band to the bottom of the conduction band, electrons are able to jump from one band to another. In order for an electron to jump from a valence band to a conduction band, it requires a specific minimum amount of energy for the transition, the band gap energy. Measuring the band gap is important in the semiconductor and nanomaterial industries. The band gap energy of insulators is large (> 4eV), but lower for semiconductors (< 3eV). A diagram illustrating the band gap is shown in Figure (2), and the band gap energies, electros and holes motilities, and electrical conductivities of intrinsic semiconductor materials at room temperature is shown in table (2).

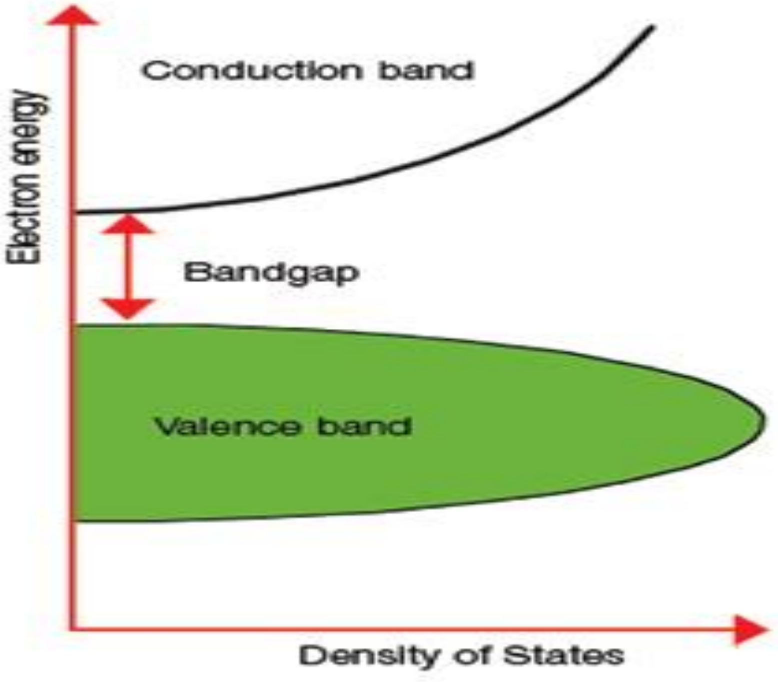
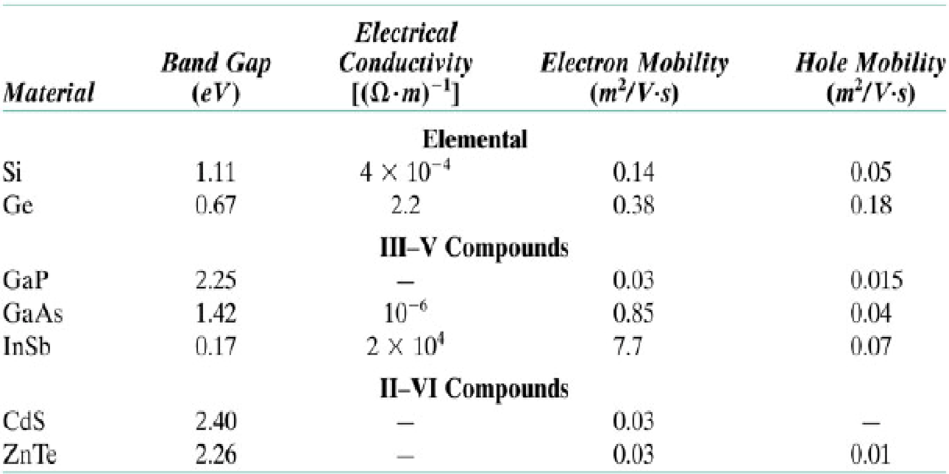


Fig. 2: A diagram illustrating the band gap

Table (2): band gap energies, electros and holes motilities, and electrical conductivities of intrinsic semiconductor materials at room temperature.



Material	*Band Gap* (*eV*)	*Electrical Conductivity* $[(\Omega\cdot m)^{-1}]$	*Electron Mobility* $(m^2/V\cdot s)$	*Hole Mobility* $(m^2/V\cdot s)$
		Elemental		
Si	1.11	4×10^{-4}	0.14	0.05
Ge	0.67	2.2	0.38	0.18
		III–V Compounds		
GaP	2.25	—	0.03	0.015
GaAs	1.42	10^{-6}	0.85	0.04
InSb	0.17	2×10^{4}	7.7	0.07
		II–VI Compounds		
CdS	2.40	—	0.03	—
ZnTe	2.26	—	0.03	0.01

V. TAUC METHOD FOR BAND GAP (Eg) MEASUREMENTS

$$\alpha = \frac{A(hv - E_g)^n}{hv}$$

Rearrange the above equation, $(\alpha\, hv)^{1/n} = A^{1/n} hv - A^{1/n} E_g$

Where $\alpha = \frac{\ln(1/T)}{x}$

α= absorption coefficient

T= Transmittance

x= Thickness of the sample

E_g = band gap of the material

n= 2, 1/2, 2/3 and 1/3 for direct allowed, indirect allowed, direct forbidden, and indirect forbidden transitions respectively.

Plotting graph of $(\alpha\, hv)^{1/n}$ Vs hv , we will get slope as $A^{1/n}$ and y intercept as $A^{1/n}E_g$. Dividing y intercept by A^n we can estimate the band gap.

VI. RESISTIVITY (ρ) OF SEMICONDUCTOR MATERIALS

Electrical resistivity of semiconductor materials are very important for making electronic devices; the purity of the material being the most important quality for this purpose. Hence to account for the purity, resistivity is taken as the parameter. The electrical resistance of a material is a basic material property. This properties of material measures conduction of an electric current in a common electrical measurement. Ohm's law and I and V relates circuit is shown in fig.(3)

Ohm's law relates the current (I) and the applied voltage (V) to the material resistance (R) as follows:

$$V = IR \qquad (1)$$

Electrical Resistivity = longitudinal electrical resistance of a uniform rod of unit length and unit cross-sectional area:

$$\rho = R\frac{A}{L} \qquad (2)$$

ρ = resistivity (Ω-cm)
R = resistance: V/I (Ω)
A = cross-sectional area of sample (cm2)
L = distance between two leads of voltmeter (cm)

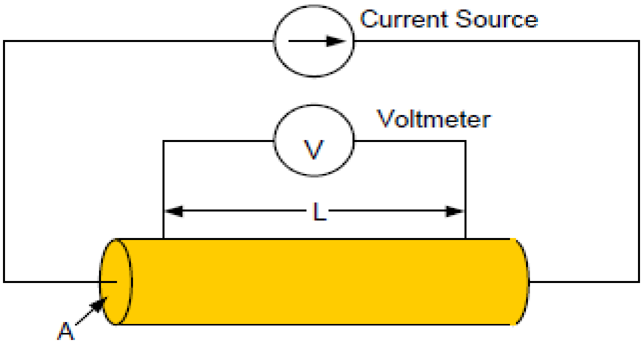


Fig. (3): Ohm's law and I and V relates circuit

The two most common methods for measuring the resistivity of semiconductor materials:

[1] FOUR PROBE METHOD-

Many conventional methods for measuring resistivity are unsatisfactory for semiconductors because metal-semiconductor contacts are usually rectifying in nature. Also there is generally minority carrier injection by one of the current carrying contacts.

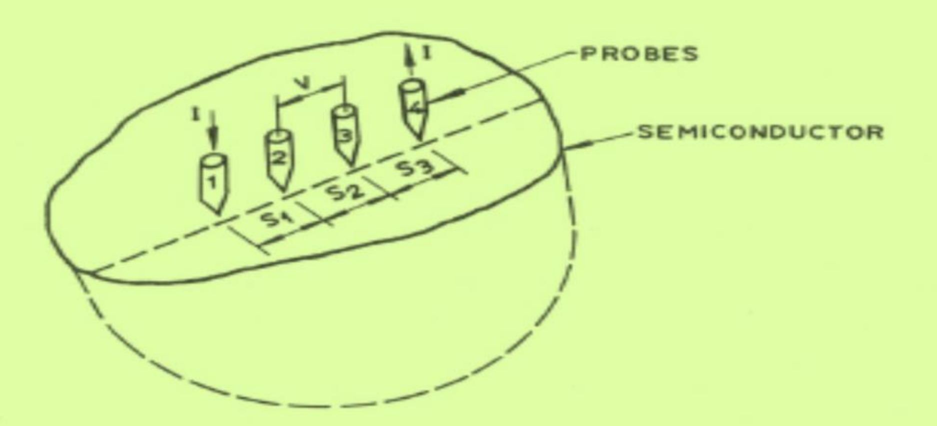


Fig. (4): Model for Four Probe Resistivity Measurements

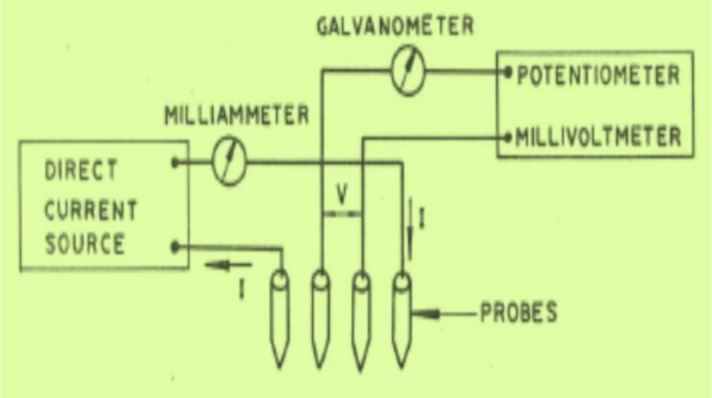


Fig. (5): Circuit for Four Probe Resistivity Measurements

An excess concentration of minority carriers will affect the potential of other contacts and modulate the resistance of the material. The method described here overcomes the difficulties mentioned above and also offers several other advantages. It permits measurements of resistivity in samples having a wide variety of shapes, including the resistivity of small volumes within bigger pieces of semiconductor. In this manner the resistivity of both sides of p-n junction can be determined with good accuracy before the material is cut into bars for making devices. This method of measurement is also applicable to silicon and other semiconductor materials. The basic model for all these measurements is indicated in Fig. (1). Four sharp probes are placed on a flat surface of the material to be measured, current is passed through the two outer electrodes, and the floating potential is measured across the inner pair. If the flat surface on which the probes rest is adequately large and the crystal is big the semiconductor may be considered to be a semi-infinite volume. To prevent minority carrier injection and make good contacts, the surface on which the probes rest, maybe mechanically lapped. The experimental circuit used for measurement is illustrated schematically in Fig. (5). A nominal value of probe spacing which has been found satisfactory is an equal distance of 2.0 mm between adjacent probes. This permit measurement with reasonable current of n-type or p-type semiconductor from 0.001 to 50 ohm-cm.

In order to use this four probe method in semiconductor crystals or slides it is necessary to assume that:

1. **The resistivity of the material is uniform in the area of measurement.**
2. **If there is minority carrier injection into the semiconductor by the current-carrying electrodes most of the carriers recombine near the electrodes so that their effect on the conductivity is negligible. (This means that the measurements should be made on surfaces which have a high recombination rate, such as mechanical lapped surfaces).**
3. **The surface on which the probes rest is flat with no surface leakage.**
4. **The four probes used for resistivity measurements contact the surface at points that lie in a straight line.**
5. **The diameter of the contact between the metallic probes and the semiconductor should be small compared to the distance between probes.**
6. **The boundary between the current-carrying electrodes and the bulk material is hemispherical and small in diameter.**
7. **The surfaces of the semiconductor crystal may be either conducting or nonconducting.**

(a) A conducting boundary is one on which a material of much lower resistivity than semiconductor (such as copper) has been plated.

(b) A non-conducting boundary is produced when the surface of the crystal is in contact with an insulator.

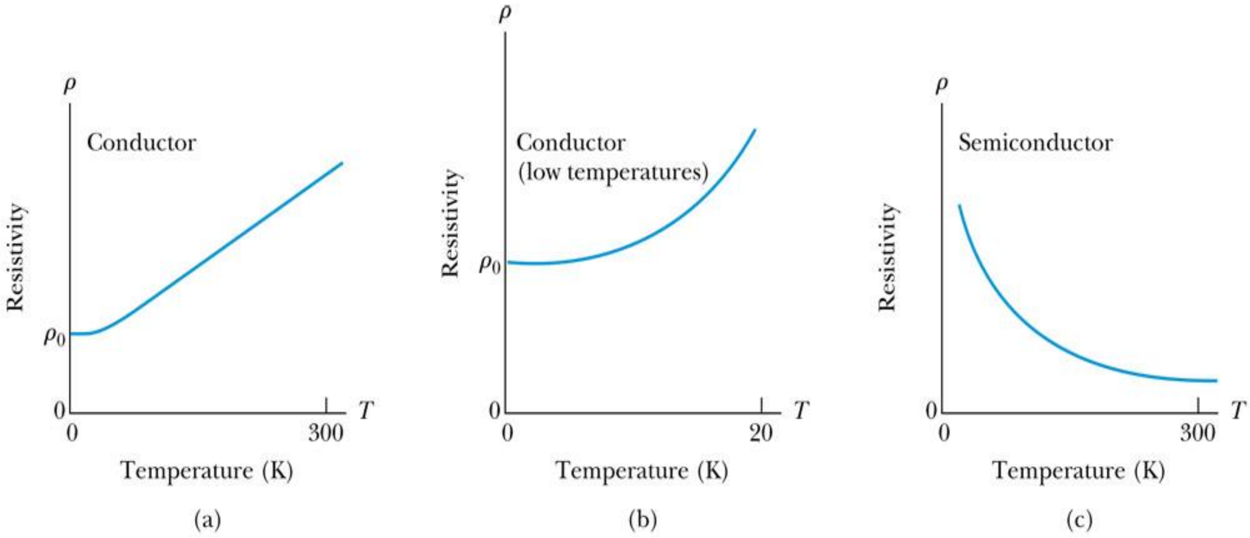
[2] VANDER PAUW RESISTIVITY METHOD-

The Vander Pauw technique, due to its convenience, is widely used in the semiconductor industry to determine the resistivity of uniform samples. As originally devised by Vander Pauw, one uses an arbitrarily shape, thin-plate sample containing four very small ohmic contacts placed on the periphery, preferably in the corners, of the plate. Van der Pauw resistivity is a 4-probe technique that involves applying a current and measuring a voltage using four small contacts on a circumference of a flat, arbitrarily shaped sample. Both of these methods use a 4-wire method to eliminate both the lead resistance and the contact resistance from affecting measurement accuracy. The electrical resistivity of solid materials span over many magnitudes. Three classifications of materials based on their resistivity is shown in Table (3).

Table (3): Typical Resistivity Values of materials

Classification	Type of Electrical Conductor	Typical Resistivities
Metals	Good electrical conductors	~10^{-6} Ω-cm
Insulators	Low electrical conductivity	~10^{9} to 10^{20} Ω-cm
Semiconductors	Intermediate levels of conductivity	~10^{-3} to 10^{7} Ω-cm

The resistivity versus temperature graph is shown in fig. (6). The resistivity versus temperature for a typical conductor is shown in fig 1(a), from this figure we notice that the linear rise in resistivity with increasing temperature at all but very low temperatures. From figure 1(b) the Resistivity versus temperature for a typical conductor at very low temperatures we notice that, we notice that the curve flattens and approaches a nonzero resistance as $T \to 0$. From figure 1(c) we notice that the resistivity versus temperature for a typical semiconductor. The resistivity increases drastically as $T \to 0$. An Electrical Resistivity and Conductivity of Selected Materials at 293K is shown in table (4).



(a) (b) (c)

Fig. (6): The Temperature Dependence of Resistivity in Semiconductors

Table (4): An Electrical Resistivity and Conductivity of Selected Materials At 293K

MATERIALS	RESISTIVITY ($\Omega - m$)	CONDUCTVITY $\Omega^{-1}\, m^{-1}$
Silver (Metal)	1.59×10^{-8}	6.29×10^{7}
Copper (Metal)	1.72×10^{-8}	5.81×10^{7}
Gold (Metal)	2.44×10^{-8}	4.10×10^{7}
Aluminium (Metal)	2.82×10^{-8}	3.55×10^{7}
Tungsten (Metal)	5.6×10^{-8}	1.8×10^{7}
Platinum (Metal)	1.1×10^{-7}	9.1×10^{6}
Lead (Metal)	2.2×10^{-7}	4.5×10^{6}
Constantan(Alloys)	4.9×10^{-7}	2.0×10^{6}
Nichrome (Alloys)	1.5×10^{-6}	6.7×10^{5}
Carbon(Semiconductors)	3.5×10^{-5}	2.9×10^{4}
Germanium (Semiconductors)	0.46	2.2
Silicon (Semiconductors)	640	1.6×10^{-3}
Wood (Insulators)	$10^{8} - 10^{11}$	10^{-8} - 10^{-11}
Rubber (Insulators)	10^{13}	10^{-13}
Amber (Insulators)	5×10^{14}	2×10^{-15}
Glass (Insulators)	$10^{10} - 10^{14}$	$10^{-10} - 10^{-14}$
Quartz –Fused (Insulators)	$7.5 - 10^{17}$	1.3×10^{-18}

VII. ADVANTAGES OF SEMICONDUCTOR DEVICES

(i) Low weight and small size
(ii) No power for the filament
(iii) Long service life (thousands of hours)
(iv) Mechanical ruggedness
(v) Low power losses and
(vi) Low supply voltages.

VIII. DISADVANTAGES OF SEMICONDUCTOR DEVICES

At the same time semiconductor devices suffer from a number of disadvantages

[i] Deterioration in performance with time (ageing); higher noise level than in electronic valvs.
[ii] Unsuitability of most transistors for use at frequencies over tens of megahertz;
[iii] Low input resistance as compared with vacuum triodes;
[iv] Inability to handle large power
[v] Deterioration in performance after exposure to radioactive emissions.

IX. CONCLUSIONS

The global consumer market wants smaller, faster, more reliable, stable, and lower-cost products. The history of semiconductors is long and complicated. Semiconductor materials are insulators at absolute zero temperature that conduct electricity in a limited way at room temperature. Conversely, silicon is robust, cheap, and easy to process, while GaAs is brittle, expensive, and insulation layers cannot be created by just growing an oxide layer; GaAs is therefore used only where silicon is not sufficient. There is no doubt that semiconductors changed the world beyond anything that could have been imagined before them. As the core technology of electronic, intelligence, integration and miniaturization of a new generation weapon, the third generation of semiconductor, which is wide band-gap semiconductor technology, gets special attention of scientists and researchers of the world. To make solar energy a possibility for the masses, scientists and researchers everywhere are trying to come up with newer and more economical ways of generating energy through solar power, especially by using various kinds of materials. Even though their efficiency and durability still remain in question, they are slowly but surely paving the way for making solar energy a viable, sustainable and prime source of energy in today's and tomorrow's world.

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