Lecture 9: Metal-semiconductor junctions

Contents

1 Introduction

Formation of electronic devices requires putting together two or more dissimilar materials (semiconductors, metals, insulators). The interface between these materials becomes crucial because it affects the electrical properties (transport) of the devices. This interface is called the *junction*. An *ideal junction* is one where there are no defects formed at the interface. Forming ideal junctions is challenging and most real materials have defects at the interface which can affect the electronic properties. But we can get an idea of the interaction between materials by studying ideal junction.

2 Metal-metal junction

Consider a junction formed between 2 metals with different work functions, as shown in figure 1. Metals are characterized by an incomplete energy band (valence and conduction band overlap) with the top of the energy band being

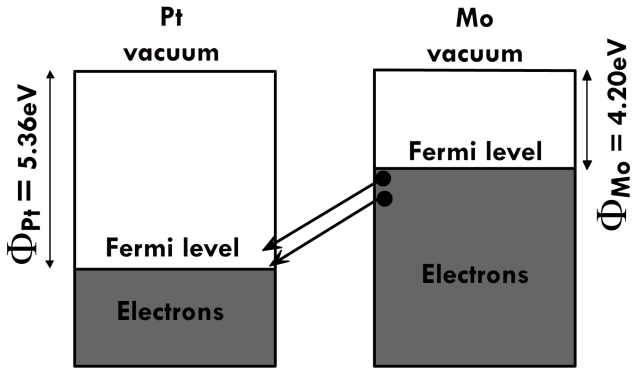

Figure 1: Junction between Mo and Pt. Mo has a smaller work function than Pt. When a junction is formed electrons from Mo move to Pt until the Fermi level lines up and the junction is in equilibrium. Adapted from *Principles of Electronic Materials - S.O. Kasap.*

the Fermi energy. The distance from the Fermi level to the vacuum level is called the *work function* (ϕ). In figure 1 the two metals are Pt and Mo with work functions of 5.36 and 4.20 eV respectively. Actual junctions are formed usually by vapor deposition of one metal on top of the other. Usually some form of post deposition annealing is also used to form the interface and reduce defect density.
The most important rule when a junction is formed is that the **Fermi levels must line up at equilibrium** (no external bias). This can be understood by using figure 1, where there are electrons in Mo at a higher energy level than those in Pt. These electrons can occupy the empty energy levels located above the Pt Fermi level. Because electrons move from Mo to Pt a net positive charge develops on the Mo side and a net negative charge on the Pt side. Thus, a *contact potential* is developed at equilibrium between the two metals. This contact potential is related to the difference in the work functions, and is shown in figure 2. For Mo-Pt junction the contact potential is 1.16 V.

2.1 Thermocouples

Metal-metal junctions are used to form thermocouples, which are used for accurate temperature measurements. Thermocouples are an example of temperature measurement by a contact technique, while pyrometers are examples

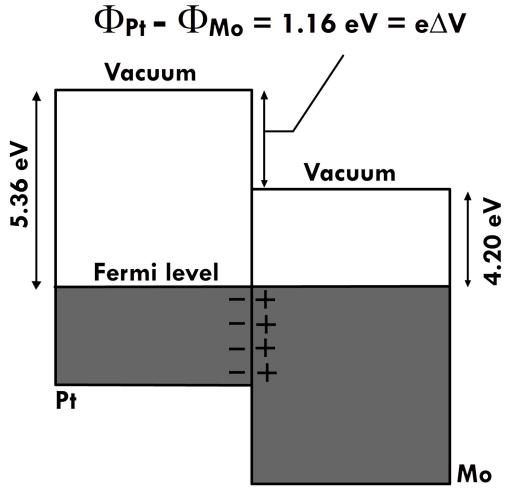

Figure 2: Junction formed between Mo and Pt at equilibrium, with a contact potential given by the difference between the work functions. The contact potential prevents further motion of electrons from Mo to Pt. Adapted from *Principles of Electronic Materials - S.O. Kasap.*

of non-contact temperature measurement. To understand the working of a thermocouple we need to consider the *Seeback effect*, summarized in figure 3. When a metal is heated at one end and the other end is kept cold, electrons at the hot end are more energetic than those at the cold end. These electrons have a greater thermal velocity and can move towards the cold end. This creates a potential within the metal with the hot end at a positive potential with respect to the cold end, see figure 3. The potential created is called the *Seeback potential* and it depends on the temperature difference between the hot and cold end.

$$\Delta V = \int_{T_1}^{T_2} S\Delta T \tag{1}$$

S is called the Seeback coefficient and is a material dependent parameter and also a function of temperature. The Seeback coefficient is approximately related to the Fermi energy by the Mott and Jones equation, which is valid for a larger number of metals.

$$S \approx \frac{\pi^2 k_B^2 T}{3eE_F}\, x \tag{2}$$

x here is a numerical constant that depends on the charge transport properties of the metal. Seeback coefficient values for different metals are listed in

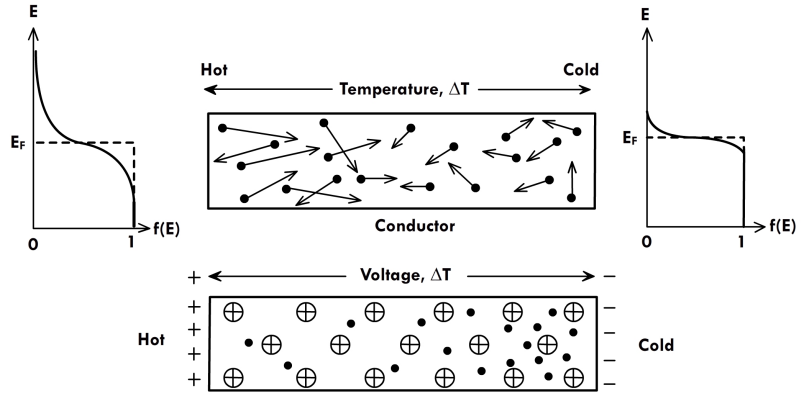

Figure 3: Schematic of the Seeback effect showing the potential development in a metal with a temperature gradient. There is a greater energy of electrons at the hot end which then flow to the cold end leasing to development on an in-built potential. The potential depends on the temperature difference and a material parameter called the **Seeback coefficient**. Adapted from *Principles of Electronic Materials - S.O. Kasap.*

table 1.

If a junction is formed between two dissimilar materials and one end is placed at the hot end (e.g. a furnace whose temperature is to be measured) and the other end placed at the cold end (room temperature) then a contact potential is developed at both ends. This contact potential is different since the Seeback coefficients of the two materials are different. So a net potential develops in the system given by

$$\Delta V \; = \; \int_{T_1}^{T_2} (S_A \; - \; S_B) \Delta T \tag{3}$$

where S_A and S_B are the Seeback coefficients of the two metals. The setup is shown schematically in figure 4. Typically, thermocouple potentials are tabulated for different temperatures for standard thermocouple materials. These tables are used when measuring the temperature of the unknown sample. There are different thermocouples used for specific temperature regions, as shown in figure 5.

3 Schottky junctions

When a metal and semiconductor are brought into contact, there are two types of junctions formed depending on the work function of the semicon-

Table 1: Seeback coefficients for some typical metals at two different temperatures and values for x. The E_F values are also listed. Adapted from *Principles of Electronic Materials - S.O. Kasap.*

Metal	**S at** 273 K ($\mu V\ K^{-1}$)	**S at** 300 K ($\mu V\ K^{-1}$)	E_F (eV)	x
Al	-1.6	-1.8	11.6	2.78
Au	1.79	1.94	5.5	-1.48
Cu	1.70	1.84	7.0	-1.79
K		-12.5	2.0	3.8
Li	14		4.7	-9.7
Mg	-1.3		3.2	1.38
Na		-5	3.1	2.2

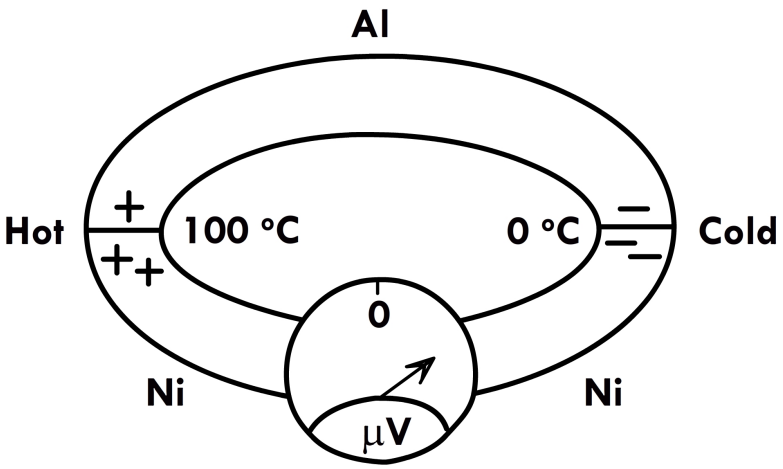

Figure 4: Temperature measurements using a thermocouple consisting of tow dissimilar metals. There is a potential difference at the two junctions arising from the different Seeback coefficients of the two materials. Adapted from *Principles of Electronic Materials - S.O. Kasap.*

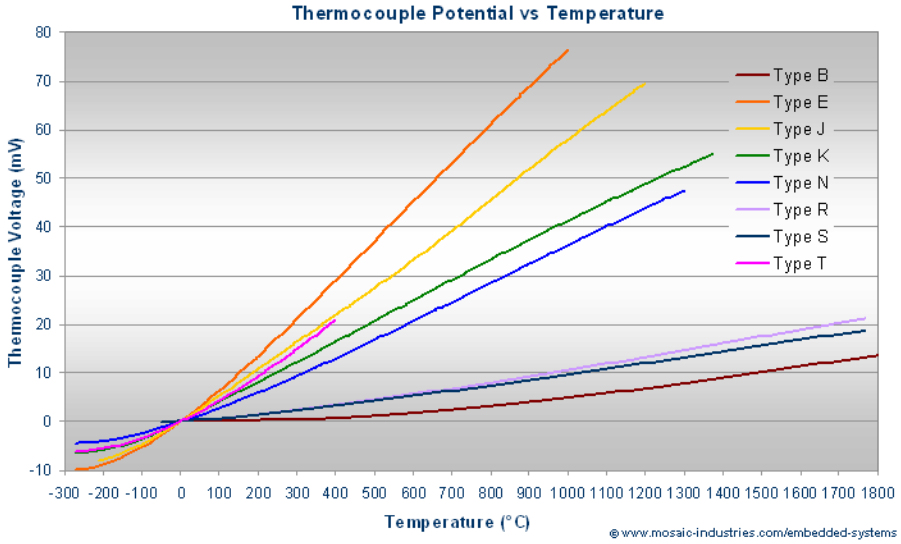

Figure 5: Thermocouple potential vs. temperature for different types of thermocouples. The potential can be measured using a standard digital voltmeter and converted into temperature. Source http://www.mosaic-industries.com/embedded-systems/microcontroller-projects/temperature-measurement/thermocouple/types-wire-element

ductor and its relation with the metal

1. Schottky junction - $\phi_m > \phi_{semi}$
2. Ohmic junction - $\phi_m < \phi_{semi}$

Consider a junction formed between a metal and n-type semiconductor, as shown in figure 6. The Fermi level of the semiconductor is higher (since its work function is lower) than the metal. Similar to a metal-metal junction, when the metal-semiconductor junction is formed *the Fermi levels must line up at equilibrium*. Another way to look at this is that there are electrons in the conduction level of the semiconductor which can move to the empty energy states above the Fermi level of the metal. This leave a positive charge on the semiconductor side and due to the excess electrons, a negative charge on the metal side, shown in figure 7, leading to a *contact potential*.

When a contact is formed between two metals, the charges reside on the surface. This is due to the high electron density found in metals (typically 10^{22} cm^{-3}). On the other hand, when a contact is formed between a metal and semiconductor, due to the low charge density on the semiconductor side (typically 10^{17} cm^{-3}) the electrons are removed not only from the surface

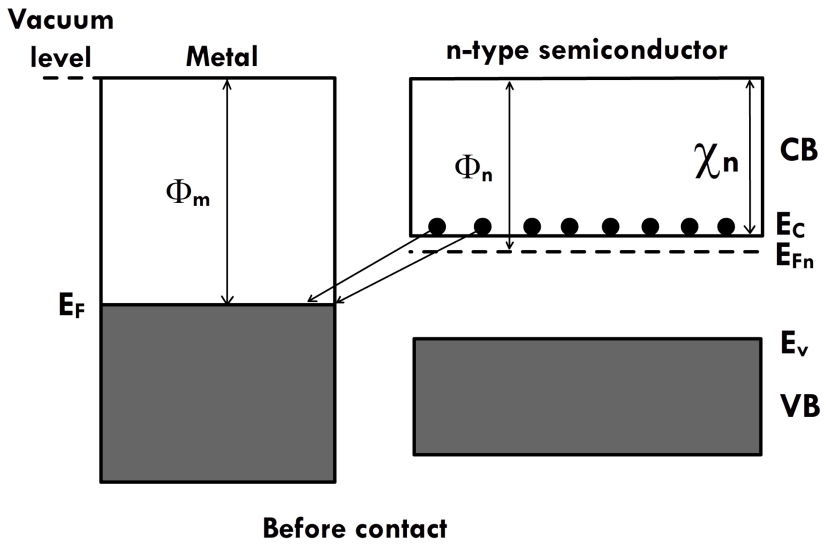

Figure 6: Schottky junction between metal and n-type semiconductor before contact. The work function of the semiconductor is smaller than the metal so that electrons can move from semiconductor to metal, forming a contact potential. Adapted from *Principles of Electronic Materials - S.O. Kasap.*

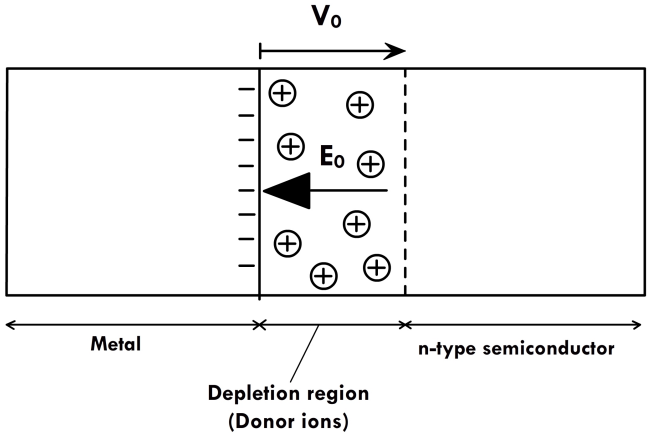

Figure 7: Schematic showing the metal, n-type semiconductor, and the Schottky junction between them. There is a depletion layer in the n-type semiconductor due to transfer of electrons to the metal. This leads to the formation of a contact potential. Adapted from *Principles of Electronic Materials - S.O. Kasap.*

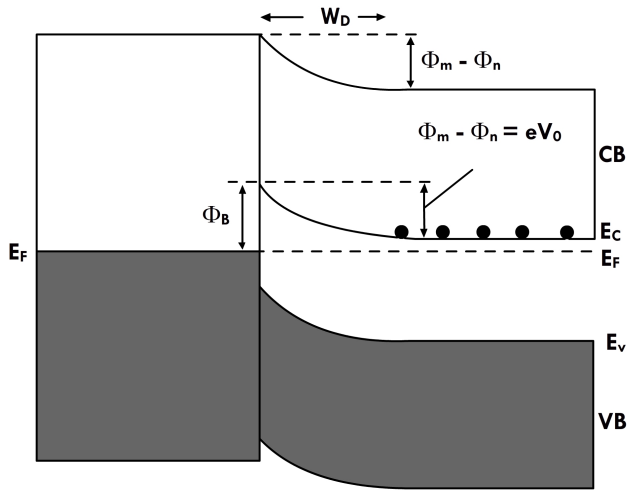

Figure 8: Schottky junction showing the band bending on the semiconductor side. Semiconductor bands bend up going from the semiconductor (positive) to metal (negative) since this is the same direction as the electric field. Adapted from *Principles of Electronic Materials - S.O. Kasap.*

but also from a certain depth within the semiconductor. This leads to the **formation of a depletion region** within the semiconductor, shown in figure 7.

Thus, when a Schottky junction is formed between the metal and semiconductor, the Fermi level lines up and also a positive potential is formed on the semiconductor side. Because the depletion region extends within a certain depth in the semiconductor there is bending of the energy bands on the semiconductor side. *Bands bend up in the direction of the electric field* (field goes from positive charge to negative charge, opposite of the potential direction). This means the energy bands *bend up* going from n-type semiconductor to metal, shown in figure 8. The Fermi levels line up and there is a certain region in the semiconductor (denoted by W) where the bands bend (this is the depletion region). Another name for the depletion region is the *space charge layer.*

There is a built in potential in the Schottky junction, V_0, and from figure 8 this is given by the difference in work functions.

$$eV_0 \; = \; \phi_m \; - \; \phi_{semi} \tag{4}$$

The work function of the metal is a constant while the semiconductor work function depends on the dopant concentration (since this affects the Fermi

level position). The contact potential then represents the barrier for the electrons to move from the n-type semiconductor to the metal. Initially, when the junction is formed electrons move to the metal to create the depletion region. The contact potential thus formed prevents *further* motion of the electrons to the metal.There is also a barrier for electrons to move from metal to semiconductor. This is called the **Schottky barrier** and denoted by ϕ_B in figure 8. This is given by

$$\phi_B \; = \; (\phi_m \; - \; \phi_n) \; + \; (E_c \; - \; E_{Fn}) \; = \; \phi_m \; - \; \chi_n \tag{5}$$

where χ_n is the electron affinity of the n-type semiconductor.
At equilibrium the motion of electrons from the semiconductor to metal is balanced by the contact potential so that there is no net current. The Schottky junction can be biased by application of an external potential. There are two types of bias

1. *Forward bias* - metal is connected to positive terminal and n-type semiconductor connected to negative terminal
2. *Reverse bias* - metal is connected to negative terminal and n-type semiconductor connected to positive terminal

The current flow depends on the type of bias and the amount of applied external potential.

3.1 Forward bias

In a forward biased Schottky junction the external potential is applied in such a way that it *opposes* the in-built potential. Since the region with the highest resistivity is the depletion region near the junction, the voltage drop is across the depletion region. *Under external bias the Fermi levels no longer line up*, but are shifted with respect to one another and the magnitude of the shift depends on the applied voltage. Energy band diagram of the Schottky junction under forward bias is shown in figure 9. Thus, electrons injected from the external circuit into the n-type semiconductor have a lower barrier to surmount before reaching the metal. This leads to a current in the circuit which increases with increasing external potential. The current in a Schottky diode under forward bias is given by

$$J \; = \; J_0 \; [\exp(\frac{eV}{k_B T}) \; - \; 1] \tag{6}$$

where J is the current density for an applied potential of V. J_0 is a constant and depends on the Schottky barrier (ϕ_B) for the system and the expression

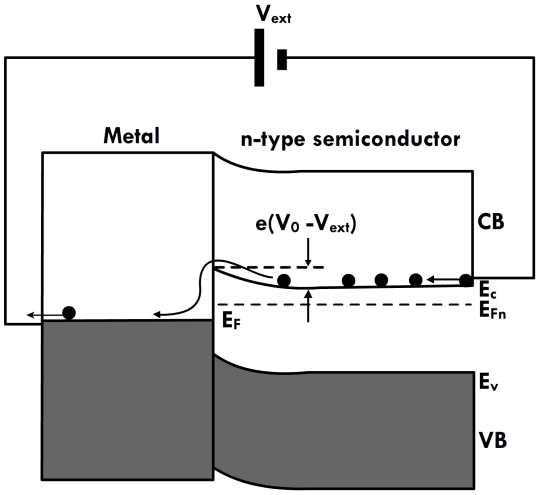

Figure 9: Schottky junction under forward bias. Adapted from *Principles of Electronic Materials - S.O. Kasap.*

is

$$J_0 \;=\; AT^2 \;\exp(-\frac{\phi_B}{k_B T}) \tag{7}$$

where A is the *Richardson constant* for thermionic emission and is a material property. Equation 6 shows that in the forward bias the current exponentially increases with applied potential.

3.2 Reverse bias

In the case of a reverse bias the external potential is applied in the same direction as the junction potential, as shown in figure 10. Once again the Fermi levels no longer line up but the barrier for electron motion from the n-type semiconductor to metal becomes higher. The electron flow is now from the metal to the semiconductor and the barrier for this is given by the Schottky barrier (ϕ_B). So there is a constant current in reverse bias, whose magnitude is equal to J_0 (as given in equation 7). From calculations it can be shown that the current in the forward bias is orders of magnitude higher than the current in reverse bias (this arises due to the exponential dependence on potential). So a Schottky junction acts as a **rectifier** i.e. it conducts in forward bias but not in reverse bias. The $I-V$ characteristics of the junction is shown in figure 11. There is an exponential increase in current in the forward bias (I quadrant) while there is a small current in reverse bias (IV quadrant).

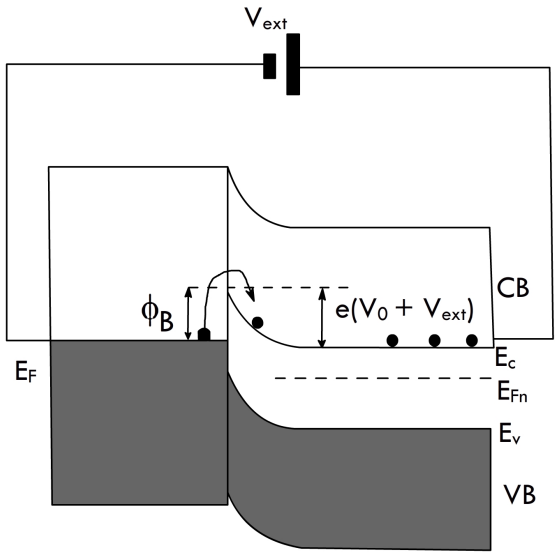

Figure 10: Schottky junction under reverse bias. Adapted from *Principles of Electronic Materials - S.O. Kasap.*

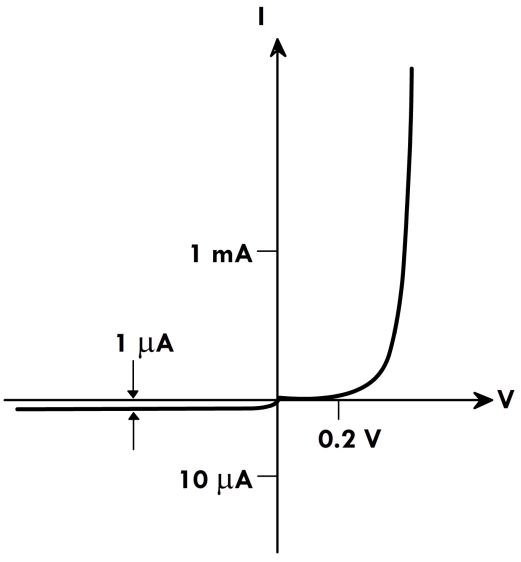

Figure 11: $I - V$ characteristics of a Schottky junction showing rectifying properties. Adapted from *Principles of Electronic Materials - S.O. Kasap.*

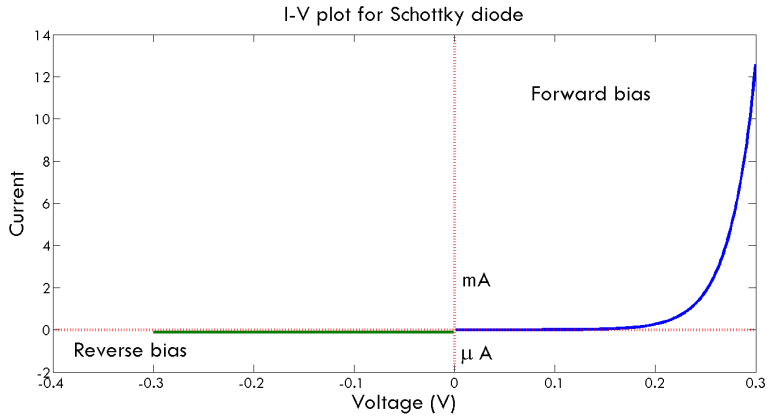

Figure 12: $I - V$ characteristics of a Schottky junction between n-Si and Au. The barrier potential energy is 0.83 eV and the Richardson constant is 110 $Acm^{-2}K^{-2}$. The plot is at room temperature and generated using MATLAB. The y-axis is in mA in the forward bias quadrant and μA in the reverse bias quadrant.

The forward and reverse bias currents for a Schottky junnction formed between Si and Au can be calculated using equations 6 and 7. Consider n-type Si with donor concentration of 10^{16} cm^{-3}. The dopant concentration fixes the Fermi level position in the semiconductor and hence its work function. For Au-Si the measured value of the Schottky barrier is 0.83 eV. The Richardson constant for this junction is 110 $Acm^{-2}K^{-2}$. Using equation 7 it is possible to calculate the reverse saturation current density in this junction. This is a constant, independent of the reverse bias voltage, and has a value of 0.12 μAcm^{-2}. The forward bias current density depends on the applied voltage, equation 6, and increases exponentially with the applied voltage. The I-V characteristics of this junction is plotted in figure 12. The plot is similar to that shown in figure 11, and rectification can be seen from the fact that forward bias current is more than three orders of magnitude higher than the reverse bias current and the value increases with applied voltage.

4 Ohmic junction

A Schottky junction is formed when the semiconductor has a lower work function than the metal. When the semiconductor has a higher work function the junction formed is called the Ohmic junction. Once again it is possible to draw the energy band diagram of the junction in equilibrium (Fermi levels line up). This is shown in figure 13. At equilibrium, electrons move

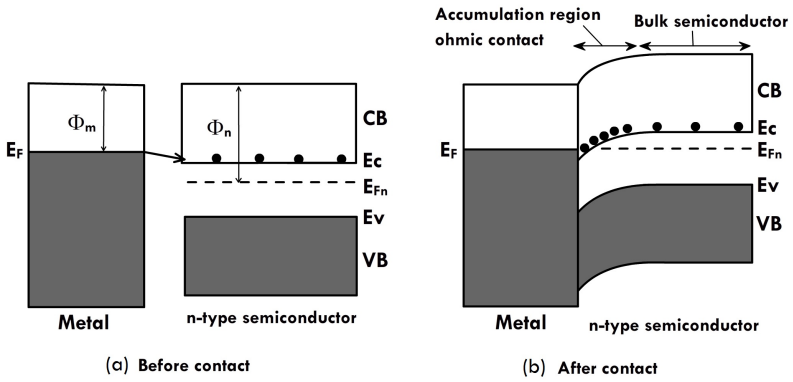

Figure 13: Ohmic junction (a) before and (b) after contact. Before contacts the Fermi levels are at different positions and they line up on contact to give an accumulation region in the semiconductor. Adapted from *Principles of Electronic Materials - S.O. Kasap.*

from the metal to the empty states in the conduction band so that there is an *accumulation region* near the interface (on the semiconductor side). The accumulation region has a higher conductivity than the bulk of the semiconductor due to this higher concentration of electrons. Thus, a Ohmic junction behaves as a resistor conducting in both forward and reverse bias. The resistivity is determined by the bulk resistivity of the semiconductor.
One of the interesting applications of Ohmic junctions is in thermoelectric devices, where a small volume can be cooled by application of direct currents. For Ohmic junctions, depending on the direction of current flow (forward or reverse biass), heat can be generated or absorbed. This is shown in figure 14. This is called **Peltier effect** and is applicable to junctions between any two dissimilar materials. So, when current flows through a metal semiconductor Ohmic junction, heat will always be released or absorbed. This can be used as a practical cooling device, as shown in the schematic in figure 15. Both p- and n- type semiconductors are used and the current flow is such that one end is always cold (heat absorbed) while the other end is hot (heat released). There are different metals that form Ohmic contacts with semiconductors. A partial list of such combinations is shown in table 2. This list is important because it gives the acceptable metals for each semiconductor that can be used in fabrication of devices. For Si, earlier Al was used for making electrical contacts, which was then replaced by Al-Cu alloys. Both form Ohmic contacts with Si. These have now been replaced by Cu (higher conductivity). But, Cu is poisonous to Si and hence cannot directly come into contact with the semiconductor. Usually, Ti or TiN is used to make electrical con-

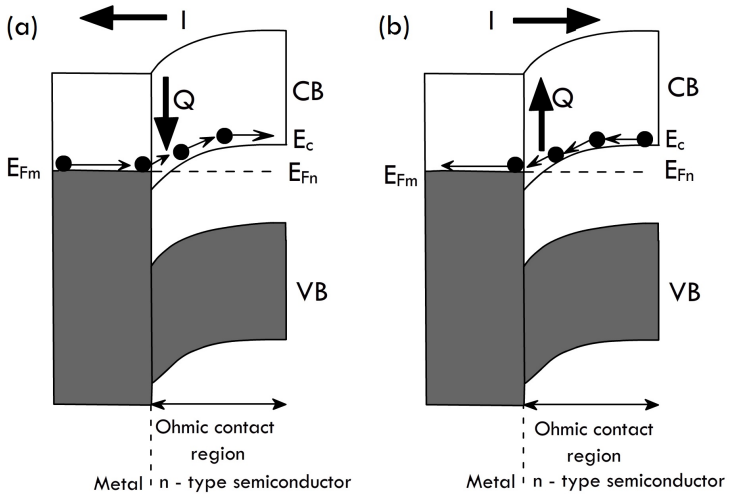

Figure 14: Current flow through an Ohmic junction can lead to heat (a) absorption or (b) release. This depends on the external bias, that determines the direction of heat flow. When electrons move from metal to higher energy levels in the semiconductor heat is absorbed and the reverse happens when electrons flow from semiconductor to metal. Adapted from *Principles of Electronic Materials - S.O. Kasap.*

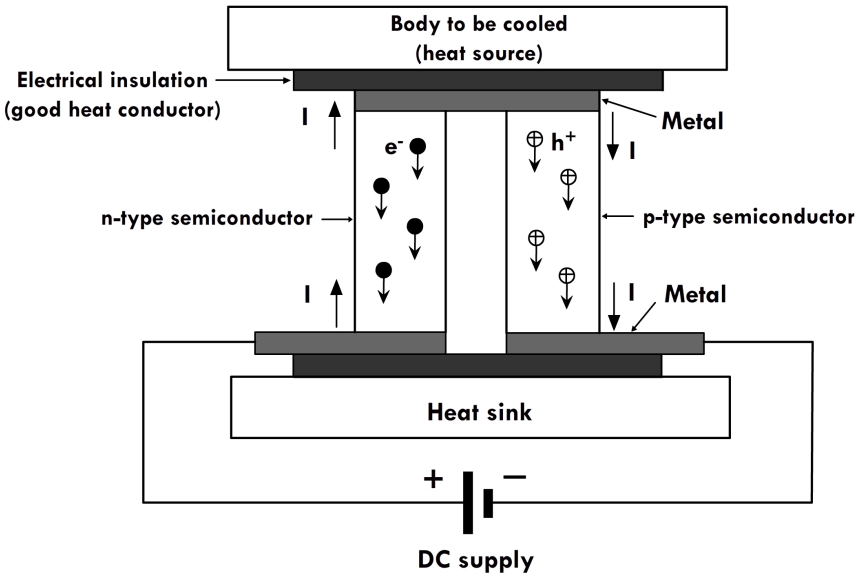

Figure 15: Schematic of the Peltier cooler using both p- and n- type semiconductors. One end of the cooler is connected to the body from which heat is absorbed (cooled) and the other end is connected to a heat sink, where it is released. Adapted from *Principles of Electronic Materials - S.O. Kasap.*

Table 2: Combination of semiconductors (n and p) and metals (alloys) that normally form Ohmic contacts. Adapted from *Principles of Electronic Materials - S.O. Kasap.*

n-semiconductor	**Metal**	**p-semiconductor**	**Metal**
Ge	Al, Au, Bi, Sb, Sn	Ge	Ag, Al, Au, Cu, Ga, In, Ni, Pt, Sn
Si	Ag, Al, Ni, Sn, In, Sb, Ti, TiN	Si	Ag, Al, Au, Ni, Pt, Sn, In, Pb, Ga, Ge, Ti, TiN
GaAs	Ag-Sn	GaAs	Ag-Zn
GaP	Al, Au-Si, Au-Sn, In-Sn	GaP	Au-Zn, Ga, Zn, Ag-Zn
GaAsP	Au-Sn	GaAsP	Au-Zn
GaAlAs	Au-Ge-Ni	GaAlAs	Au-Zn
InAs	Au-Ge, Sn	InAs	Al
InGaAs	Au-Ge, Ni	InGaAs	Au-Zn, Ni
CdS	Ag, Al, Au, Ga, In		
CdTe	In	CdTe	Au, In-Ni, Pt, Rh
ZnSe	In, In-Ga, Pt		
SiC	W	SiC	Al-Si, Si, Ni

tact with Si, and then Cu is deposited. Ti or TiN is chosen because it also forms Ohmic contacts with p and n type Si, see table 2, and can be easily deposited by chemical vapor deposition. For integrated devices electrical contacts to the outside circuit components are done using evaporated metals and Ohmic contacts are formed. This is because the electrical contact should not impose a rectifying behavior on the device. Thermal processing of metal-semiconductor contacts can lead to inter-diffusion and formation of metal silicides. Pt-Si forms a number of silicide phases like PtSi, Pt_2Si, and Pt_3Si. Similarly, Ti-Si forms $TiSi_2$, Ti_2Si, and Ti_3Si. Thus the contact is no longer between a metal-semiconductor but between a silicide-semiconductor. This can affect the electrical properties of the junction.