ACTIVATION ENERGY

Activation energy is defined as the excess energy over the ground state which must be acquired by an atom or molecular system in order that a particular process can occur. This excess energy is actually the change in total Gibbs free energy in the process. Few examples are the energy needed by a molecule to take part in chemical reaction, by an electron to be excited from valence band or from an impurity band to conduction band or a lattice defect to move to a particular neighboring site. Activation energies involved in the three processes in semiconductor, namely, activation energy of ionization of impurities, activation energy for diffusion, and activation energy for the current transport in metal–semiconductor rectifying contact (Schottky contact) will be discussed here.

In the context of semiconductors the activation energy for ionization of impurities or native point defects (donor or acceptor) can be treated with the law of mass action which otherwise is applied to chemical reaction. For example, energetics of a chemical reaction between two starting reagents A and B, which give rise to two products C and D is characterized by change in Gibbs free energy ΔG (1)

$$A + B \xrightarrow{\Delta G} C + D \tag{1}$$

where $\Delta G = \Delta E + P\Delta V - T\Delta S$, P is pressure, and ΔE, ΔV, ΔS are change in energy, volume, and entropy, respectively. In the case of electronic reaction, change in volume (ΔV) and change in entropy (ΔS) can be neglected. In this case $\Delta G \approx \Delta E$. From the law of mass action it can be shown through the principle of detailed balance (1)

$$\frac{[C][D]}{[A][B]} = K \exp\left(-\frac{\Delta E}{k_B T}\right) \tag{2}$$

where $[A]$, $[B]$, $[C]$, $[D]$ are concentrations of reagents and products, and K is constant. For semiconductors ΔE is defined as activation energy of the electronic reaction inside solid state. For example, in the case of intrinsic semiconductors, an electron hole pair can be generated either by thermal or optical excitation. Hence the band gap energy E_g is the relevant activation energy for electron–hole ionization in intrinsic semiconductors.

$$VE \overset{E_g}{\longleftrightarrow} e^- + h^+ \tag{3}$$

where VE stands for valence electron. If n and p are the concentration of electrons and holes, respectively, from the law of mass action we can get

$$np = C \exp\left(-\frac{E_g}{k_B T}\right) \tag{4}$$

where k_B is the Boltzmann constant and $C = N_c N_v$, where N_c, and N_v are densities of states in the conduction band and valence band, respectively.

ACTIVATION ENERGY OF IONIZATION

In the case of extrinsic semiconductor the ionization process can be represented by

$$D_0 \overset{E_D}{\longleftrightarrow} D^+ + e^- \tag{5}$$

where D_0 and D^+ stand for neutral and ionized donor with concentration N_{D_0} and N_D^+, respectively, n is the electron concentration, and ionization energy, E_D is the activation energy of this process. From the law of mass action

$$\frac{nN_D^+}{N_{D_0}} = C\exp\left(-\frac{E_D}{k_BT}\right) \tag{6}$$

If we assume $N_D \gg n$ (which is the case at low temperature), it can be shown (2)

$$n^2 = \frac{1}{2}N_DN_c\exp\left(-\frac{E_D}{k_BT}\right) \tag{7}$$

The above treatment is not valid in case of two donor species with different activation energies. The free electron concentration in n-type semiconductor having two different donors is given by

$$n = N_{D1}^+ + N_{D2}^+ \tag{8}$$

where N_{D1}^+ and N_{D2}^+ are the donor concentrations. From Fermi-Dirac statistics, it can be shown (2)

$$N_{D1}^+ = N_{D1} - \frac{N_{D1}}{1+\dfrac{1}{g}\exp\left(\dfrac{E_{D1}-E_F}{k_BT}\right)} \tag{9}$$

$$N_{D2}^+ = N_{D2} - \frac{N_{D2}}{1+\dfrac{1}{g}\exp\left(\dfrac{E_{D2}-E_F}{k_BT}\right)} \tag{10}$$

where E_{D1} and E_{D2} are the activation energies of donors in semiconductor and we can assume $E_{D2} > E_{D1}$. g is the degeneracy of the ground state of the donors.

At low temperature when deep donors with activation energy E_{D2} is neutral, activation energy E_{D1} of the shallow donor can be determined [Eq. (7)] using relation

$$n = \left(\frac{1}{2}N_{D1}N_c\right)^{1/2}\exp\left(-\frac{E_{D1}}{2k_BT}\right) \tag{11}$$

As the temperature is increased, deep donors start to emit electrons to conduction band and become ionized. From Eqs. (8–10) we can get

$$\begin{aligned}(N_{D2}^+)^2 + N_{D2}^+\left[N_{D1}^+ + \frac{1}{g}\exp\left(-\frac{E_{D2}}{k_BT}\right)\right]& \\ - \frac{1}{2}N_{D2}N_c\exp\left(-\frac{E_{D2}}{k_BT}\right) &= 0\end{aligned} \tag{12}$$

If $N_{D1}^+ \gg 1/g\ N_c\exp(-E_{D1}/k_BT)$, which is typically the case at higher temperature, it can be shown (2)

$$n(n-n_{D1}) = \frac{1}{2}N_{D2}N_c\exp\left(-\frac{E_{D2}}{k_BT}\right) \tag{13}$$

Now the above relation can be used to find out activation energy of the deep donor, E_{D2}. Similar treatment can be done for ionization energy for acceptors.

Most of the impurities belonging to group V (for donors) and III (for acceptors) of the periodic table in Si and group II (for acceptors) and IV (for donors) in GaAs are the substitutional type. When an impurity is introduced in a crystal, the periodicity of the crystal is perturbed. The potential created by the impurity at the atomic site becomes more important than the background potential of the host lattice. If the perturbed potential is long range and the interaction between impurity and host lattice is weak, the impurity potential can be treated in the framework of effective mass theory (2). In this case band edge states are used to calculate the dopant activation energy and the impurity atoms are called *shallow dopants*. An estimate of the binding energy of the outermost electron in the shallow dopants can be made by a simple hydrogen atom model. The donor atom could be a pentavalent atom P in Si or a Si in Ga site of GaAs. The donor ion has a charge of unity and the interaction between electron and ion is coulombic attraction suppressed by the dielectric constant of the material. From elementary quantum mechanics, we get the effective mass equation of donor energy level

$$\left[-\frac{\hbar^2}{2m_e^*}\nabla^2 + \frac{e^2}{\epsilon_s r}\right]\phi(r) = E\phi(r) \tag{14}$$

$$E = E_c - \frac{e^2m_e^*}{2\epsilon_s^2\hbar^2n^2},\ n = 1, 2, 3, \ldots \tag{15}$$

where m_e^* is the effective mass of electron, m_e the mass of electron, and ϵ_s the dielectric constant of the material. The donor ionization energy E_D is required for a transition from $n = 1$ to $n \to \infty$ and is given by

$$E_D = \frac{m_e^*}{m_e\epsilon_s^2}\,13.6\,eV \tag{16}$$

For example, E_D for P in Si is 45 meV and E_D for Si in GaAs is 5.8 eV. Similar treatment can be applied for shallow acceptors in semiconductors.

Coulomb potential due to shallow impurities overlap as doping concentration increases and electrons can move from one donor to another donor either by tunneling or by thermal jump. The probability of these two processes increases with increasing doping concentration which in effect lowers the activation energy. The semiconductor behaves as a metal in extreme cases, where activation energy becomes zero because of the high doping. Phenomenologically, the dependence of the activation energy on the concentration of the dopants can be given as (2,3)

$$E_D = E_{D_0}\left[1-\left(\frac{N_D}{N_{\text{crit}}}\right)^{1/3}\right] \tag{17}$$

where E_{D_0} is the activation energy when $N_D \ll N_{\text{crit}}$. The insulator-to-metal transition occurs when the distance between two impurity atoms becomes comparable to the Bohr radius, which is called the Mott criterion for metal–insulator transition. Mott critical density (N_{crit}) of dopants can be given by the relation (3)

$$a_B^* N_{\text{crit}}^{1/2} = 0.25 \tag{18}$$

where a_B^* is the effective Bohr radius.

The dopant atom which gives rise to a shallow level can be treated with simple effective mass theory, because the perturbation created by a shallow impurity is weak and long range. In case of certain types of defects the perturbation can be strong and short range. This type of defect can arise from a missing atom or chemical impurity or any complex. This type of impurity is called a deep impurity, which gives rise to an energy level deep in the band gap (4). This deep energy level can produce trapping or recombination centers which have an important role in semiconductor-based devices. For example, Au in Si produces two deep levels: an acceptor-like state at 0.54 eV below the conduction band and a donor-like state at 0.35 eV above the valence band. The 0.54 eV deep level is the recombination center and has been used to increase the speed of the Si-based bipolar device. EL_2 is a very important defect complex in GaAs, which is the As–antisite–Ga vacancy complex (5). EL_2 gives a deep donor level at 0.76 eV below the conduction band edge and makes GaAs semi-insulating. Semi-insulating GaAs is extremely important for GaAs-based electronic devices. Another extremely important deep level is $Al_xGa_{1-x}As$ which is the DX center (5). DX center is a donor-related deep level which is found in several ternary alloys when these are doped with either group IV (Si, Ge, Sn) or group VI (S, Se, Te) dopants. The shift in threshold voltage and transient in the source-to-drain current and collapse of current–voltage characteristics at low temperature in GaAs-$Al_xGa_{1-x}As$-based high electron mobility transistor and instabilities in the laser output are the few problems due to the presence of DX center in GaAs and $Al_xGa_{1-x}As$.

Determination of ionization energy of dopants which give rise to deep levels requires detailed quantum mechanical analysis including band structure of the semiconductor. The results cannot be generalized in a simple form, as is possible for shallow impurities. State-of-the-art theoretical techniques, such as the supercell technique, are routinely used for this problem (5). Figure 1 gives the activation energies of shallow levels and deep levels in Si, Ge, and GaAs.

EXPERIMENTAL DETERMINATION OF ACTIVATION ENERGY FOR IONIZATION

Photoluminescence (PL) is the most popular optical characterization technique for determination of optical ionization energy. It is very efficient technique for shallow impurities. PL can detect simultaneously many impurities, which give rise to radiative recombinations. At low temperature the sample is exited with laser with $h\nu > E_g$ for creating electron–hole pairs. These electron–hole pairs recombine through different parallel mechanisms. At room temperature band-to-band recombination is dominant, but at low temperature exitonic and donor or acceptor-free carrier recombination is dominant. In the case of direct band-gap semiconductor, the emitted photon energy for free and bound exitons can be given, respectively,

$$h\nu = E_g - E_{FE} \tag{19}$$

$$h\nu = E_g - E_{BE} \tag{20}$$

where E_{FE} is the free exitonic energy and E_{BE} is bound exitonic energy. In the case of a bound exiton, a free electron can recombine with a hole on a neutral acceptor, or a free hole can recombine with an electron on a neutral donor. In the case of an indirect band-gap semiconductor, free exitonic and bound exitonic transitions are phonon-assisted for momentum conservation, and emitted photon energy in this case can be given by

$$h\nu = E_g - E_{FE} - E_p \tag{21}$$

$$h\nu = E_g - E_{BE} - E_p \tag{22}$$

where E_p is the phonon energy. The ionization energy of shallow impurities E_D can be found out from Haynes's rule (2) and can be represented as

$$E_{FE} - E_{BE} = \alpha (E_D)^n \tag{23}$$

where α and n are constants with typical values of 0.05 to 0.5 and 1.0 to 2.0, respectively. For acceptors in Si it was found $\alpha = 0.1$ and $n = 1.0$.

Besides free and bound exitonic transitions, other dominant transitions are electron–acceptor (eA^o), donor–hole (D^oh), and donor–acceptor (D^oA^o). The emitted photon for these three transitions are given by

$$h\nu = E_g - E_D \tag{24}$$

$$h\nu = E_g - E_A \tag{25}$$

$$h\nu = E_g - E_A - E_D + \frac{e^2}{4\pi\epsilon_s r} \tag{26}$$

where $e^2/4\pi\epsilon_s r$ is coulombic interaction between acceptor and donor and r is the distance between acceptor and donor. The relations, Eqs. (24) to (26), can be used directly for determining shallow impurity ionization energy. At finite temperatures $\frac{1}{2}k_BT$ should be added to the right-hand side of Eqs. (19) to (22) and (24) to (26).

The most common electrical characterization technique for measuring the thermal activation energy of shallow impurities is temperature-dependent Hall measurements. As the temperature increases, the extrinsic semiconductor shows three regions which are the carrier freeze-out, the saturation, and intrinsic regions. The activation energy is evaluated from the carrier freeze-out regime. The electron concentration (n) in n-type semiconductors is measured through the Hall coefficients R_H ($= -1/en$). The dependence of n on temperature is given by Eq. (7). The thermal activation energy of either donor or acceptor can be determined from the slope of n versus $1/T$ straightline using the following relation

$$E_D = -2k_B \frac{d(\log_e n)}{d(1/T)} \tag{27}$$

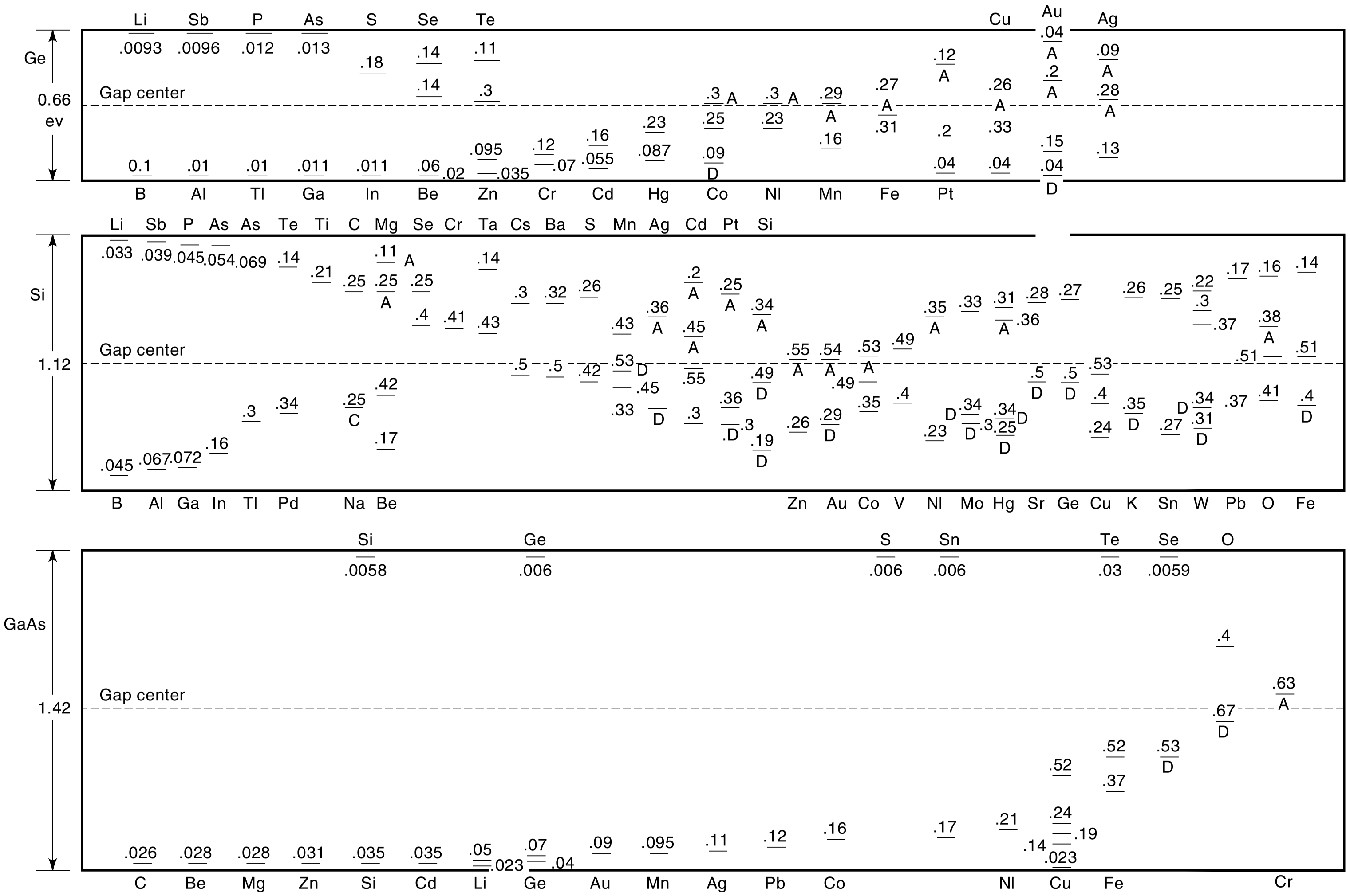

Figure 1. Ionization energies (in eV) of different shallow and deep impurities in Ge, Si, and GaAs (from Ref. 9).

In the case of a compensated semiconductor-like GaAs, where $n = N_D^+ - N_A^-$, the slope of the straightline becomes half of that of an uncompensated semiconductor, which is

$$E_D = -k_B \frac{d(\log_e n)}{d(1/T)} \tag{28}$$

Deep level transient spectroscopy (DLTS) is one of the most powerful methods for detecting and characterizing defect-related deep levels in semiconductors. Its major strength is that it is spectroscopic, that is, it gives a unique peak for each deep level detected. Quantitative information is obtained from the spectra with a small amount of analysis.

DLTS exploits the properties of a potential barrier in a Schottky diode or *p–n* junction for the detection of deep levels. A nonequilibrium situation is created by applying a forward bias for a short duration, during which the depletion width reduces and the trap level goes below the Fermi level and the unoccupied traps capture electrons from conduction band. On application of the reverse bias, these traps emit electrons to the conduction band. The key to the DLTS measurement is that as the electrons are emitted to the conduction band they leave behind a net positive charge and capacitance of the diode changes with time. Hence the relaxation of the occupied traps can be monitored by measuring the capacitance transient given by Refs. 5 and 6.

$$C(t, T) = C_o\left[1 - \frac{N_T}{2N_D}\exp(-e_n t)\right] \tag{29}$$

where C_0 is zero bias capacitance of the Schottky diode, N_T is the concentration of the defects which give rise to a deep level inside the forbidden gap of the semiconductor, N_D the concentration of the donors, and e_n is the emission rate of the deep center, which has an Arrhenius dependence on temperature.

$$e_n = AT^2 \exp\left(-\frac{E_T}{k_B T}\right) \tag{30}$$

where E_T is the emission activation energy of the deep level and A is related to the capture cross section of the trap.

In DLTS, capacitance transient signal $C(t, T)$ is converted into a DLTS spectrum by a signal processing technique, in which the temperature-dependent DLTS signal $S(T)$ is constructed from the capacitance transient $C(t, T)$ at a fixed rate window t_1, t_2 and given by

$$S(T) = C(t_1, T) - C(t_2, T) \tag{31}$$

The signal $S(T)$ has a maximum at a temperature $T_{\max}$ and the emission rate at the maximum can be given by

$$e_n = \frac{\ln(t_2/t_1)}{t_2 - t_1} \tag{32}$$

From different choices of the rate window, the dependence of the emission rate on temperature can be obtained. The intensity of the DLTS peak is related to the concentration of the deep centers. Essentially, we can determine all parameters of the deep impurity center (activation energy, capture cross section, concentration) from the DLTS spectra.

ACTIVATION ENERGY OF DIFFUSION

Diffusion describes the different ways by which foreign atoms move inside material. Controlled amounts of chemical impurities in semiconductors and insulators can considerably change the electrical properties. Knowledge of diffusion of different atoms provides the technology, by which the material properties can be controlled. At present, diffusion is a basic process step in the fabrication of discrete devices and integrated circuits (7). Diffusion had been studied extensively in solid-state physics before the discovery of *p–n* junctions. Essentially there are three basic processes by which impurities diffuse through the semiconductor. Those are

1. *Interstitial Diffusion.* In this case impurity atoms move inside the material by jumping from one material site to another site.
2. *Substitutional Diffusion.* This is similar to interstitional diffusion except that impurity atoms move from one substitutional site to another.
3. *Interchange Diffusion.* In this case two or more impurity atoms move by exchanging their respective positions inside the solid.

Activation energy in all the above-mentioned diffusion processes can also be explained through law of mass action. In the case of diffusion processes the relevant activation energy is the potential barrier E_{diff} that has to be overcome by the impurity atom while hopping from one interstitial site to another interstitial site or one substitutional site to another site. If the probability of jump is proportional to $\exp(-E_{\text{diff}}/k_B T)$, the diffusion coefficient D can be defined as

$$D = a^2 f \tag{33}$$

where a is the average hopping length, $f = f_0 \exp(-E_{\text{diff}}/k_B T)$, is the rate of successful diffusion hops, and f_0 is the frequency of lattice vibration. The diffusion coefficient D can now be given by

$$D = D_0 \exp\left(-\frac{E_{\text{diff}}}{k_B T}\right) \tag{34}$$

where $D_0 = a^2 f_0$.

Table 1. Activation Energies of Important Dopants and Transition Metals in Si (From Ref. 7)

Impurity	P	As	Sb	B	Al	Ga	Au	Cu	Fe	Ni	O
$E_{\text{diff}}(eV)$	3.66	3.44	3.65	3.46	3.41	3.39	1.12	1.00	0.87	1.40	2.44

Table 2. Activation Energies of Important Dopants and Transition Metals in GaAs (From Ref. 7)

Impurity	Au	Be	Cr	Cu	Li	Mg	Mn	O	S	Se	Sn
$E_{\text{diff}}(eV)$	2.64	1.20	3.40	0.53	1.00	2.70	2.49	1.10	2.60	4.16	2.70

EXPERIMENTAL DETERMINATION OF ACTIVATION ENERGY FOR DIFFUSION

In order to determine the activation energy for diffusion, the profile of the dopant distribution and the evolution of the profile and annealing at different temperatures are determined. Either diffusion from external sources or diffusion inside implanted samples are studied. The profile of the impurity is determined generally by secondary ion mass spectroscopy (SIMS) and Rutherford back scattering (RBS). The dopant profile in semiconductors is also measured by a simple capacitance–voltage or electrolytic capacitance–voltage method. Table 1 gives the activation energies for diffusion for important impurities in Si. Table 2 gives the activation energies of important impurities in GaAs.

ACTIVATION ENERGY OF CURRENT TRANSPORT THROUGH METAL–SEMICONDUCTOR CONTACT

The current transport in an intimate metal–semiconductor contact is due to majority carriers. The mechanism for current transport in case of a metal–semiconductor rectifying Schottky diode can be explained by thermionic emission theory (8). A potential barrier seen by electrons in metal is considered to be activation energy in this current transport process. The current–voltage relation for the current transport through the metal–semiconductor structure is given by

$$J = A^{*}T^{2}\exp\left[-\frac{e\phi_B}{nk_BT}\right]\left[\exp\left(\frac{eV}{nk_BT}\right)-1\right] \tag{35}$$

where A^{*} called the effective Richardson constant. V is the applied bias and n is called ideality factor. ϕ_B is the Schottky barrier and can be represented by

$$\phi_B = \phi_m - \chi \tag{36}$$

where ϕ_m is the metal work function and χ, the electron affinity of the semiconductor. There are several effects which can modify the theoretical ϕ_B given in Eq. (36). ϕ_B depends on bias and temperature. The simple effect of bias on ϕ_B can be described by image force lowering. The change in ϕ_B due to the image force can be given by

$$\Delta\phi = \sqrt{\frac{eE}{4\pi\epsilon_s}} \tag{37}$$

where E is the electric field due to the image charge. Figure 2 shows experimental values of ϕ_B for different metals on Si and GaAs. It is clear from Fig. 2 that the variation for ϕ_B in case of Si more or less follows Eq. (36). In the case of GaAs, ϕ_B does not vary with the work function of the metal, which is called *Fermi level pinning.*

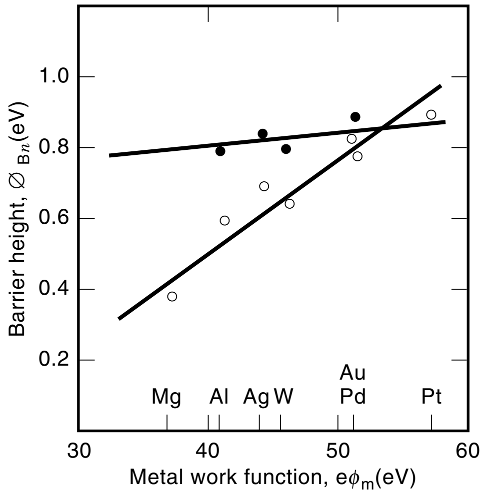

Figure 2. Schottky barrier heights for Si and GaAs versus work functions of different metals (from Ref. 10).

EXPERIMENTAL DETERMINATION OF ACTIVATION ENERGY FOR SCHOTTKY BARRIER

There are three methods for determining the Schottky barrier, which are the temperature dependent current–voltage method, capacitance–voltage method, and photocurrent method. The thermionic current–voltage characteristic of a Schottky diode can be given by [from Eq. (35)]

$$I = I_S\left[\exp\left(\frac{eV}{nk_BT}\right)-1\right] \tag{38}$$

where I_S is the saturation current

$$I_S = AA^{*}T^{2}\exp\left(-\frac{e\phi_B}{nk_BT}\right) \tag{39}$$

where A is the area of the Schottky contact. The constant I_S at different temperatures is determined by an extrapolation of the log(I) versus V curve at $V = 0$. The barrier height ϕ_B is calculated using the Eq. (39). From Eq. (39), we can get

$$\phi_B = \frac{k_BT}{e}\ln\left(\frac{AA^{*}T^{2}}{I_S}\right) \tag{40}$$

The capacitance of a Schottky diode based on an n-type semiconductor is given by

$$C = \sqrt{\frac{e\epsilon_s A^2 N_D}{2\left(V_{bi} + |V| - \dfrac{k_B T}{e}\right)}} \tag{41}$$

where V_{bi} is the built in voltage. ϕ_B is related to the built-in voltage by the relation

$$\phi_B = V_{bi} + \frac{k_B T}{e} \ln\left(\frac{N_C}{N_D}\right) \tag{42}$$

If $1/C^2$ is plotted against V we get the value of $2/eA^2\epsilon_S N_D$ from the slope and $-V_{bi} + k_B T/e$ from the intercept. Knowing N_D from the slope and V_{bi} from intercept, ϕ_B can be found out from the Eq. (42).

In the photocurrent method, the carrier from the metal side of the Schottky diode can be exited to the semiconductor overcoming the barrier by sub-band gap length. Electron emission is possible if $h\nu > \phi_{B.}$ The yield Y can be defined as the ratio of the photocurrent to the absorbed photon flux and given by,

$$Y = B(h\nu - e\phi_B)^2 \tag{43}$$

where B is constant. Plotting $Y^{1/2}$ versus $h\nu$ gives $\phi_{B.}$

Activation energies involved in several other processes are not discussed here. For example, activation energy for electron or hole capture (E_c) by a defect from conduction band or valence band, respectively, is very important in the context of deep level center in semiconductor. E_c can be as large as activation energy for electron or hole emission by a defect, which is the case for DX center in III–V semiconductors. Origin of activation energy in different processes has been discussed phenomenologically. Discussion of first principle theory of the origin of activation energy is beyond the scope of this article.

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