Chapter II

THEORY OF PHOTOEMISSION OPTOGALVANIC EFFECT

An outline of the photoemission optogalvanic (POG) effect has been given in the previous chapter. Theoretical treatment of POG effect is presented in this chapter.

2.1. Electron Emission from Metal Surfaces

Creation of electron beams from metal surfaces are of considerable interest due to their relevance both in fundamental and applied fields [1-8]. The principal methods employed for this purpose are thermionic emission, field emission and photoemission.

For electrons to be torn away from metal surfaces they should be loosely bound to it. For the free electrons, the interior of a metal may be considered as an equipotential volume, but there is a potential barrier at the surface. When the electron reaches the surface of the metal, it collides with the potential energy barrier. At absolute zero temperature, it is impossible for an electron to escape from the metal because this requires an amount of energy equal to potential barrier and the maximum energy

possessed by any electron is only Fermi energy. It is necessary to supply an additional amount of energy equal to the difference between the potential barrier energy and Fermi energy in order to make this escape possible. This difference is known as the workfunction and it is the minimum amount of energy that must be given to the fastest moving electron at the absolute zero of temperature in order for this electron to be able to escape from the metal. Workfunction of a metal may be interpreted in another way [10] as, when a negative electron escapes the metal surface it will induce a positive charge on a metal from which it escapes. There will then be a force of attraction between the induced charge and the electron. Unless the electron possess sufficient energy to carry it out of the region of influence of this image force of attraction it will be returned to the metal.

2.1.1. Thermionic Emission

In thermionic emission, thermal energy is supplied to the electron from the lattice of the heated metal crystal. The energy distribution of electrons changes because of the increased temperature. Electrons achieving energies greater than the potential barrier energy may be able to escape from the metal. The thermionic current is given by the Richardson equation

$$I = S\ A_0 T^2\ E^{-E\omega/kT} \qquad (2.1)$$

where S- area of filament, A_0- a constant, T - temperature, k - Boltzmann's constant, E_ω - workfunction.

2.1.2. Field Emission

Under normal operating conditions, the field applied between the cathode and the collecting anode is accelerating rather than retarding, and hence the field aids the electrons in overcoming the image force at the surface of the metal. When the accelerating field at the surface of a cold cathode is very intense it will lower the potential energy barrier at the surface of the cathode [10] and also it is reduced in the thickness. For fields of the order of millions of volts per meter, the barrier may become so thin that the electron considered as a de-Broglie wave, may penetrate or tunnel through the barrier.

2.1.3. Photoemission

By the application of light, electron emission from metal surfaces can be achieved. It was Hertz in 1887 [11] who first documented observation of photoelectric effect. Subsequent investigators, principally by J.J.Thomson [12]

and H.Lenard [13-15] identified photoelectric process with the emission of electrons and established that the velocity of the emitted electron depend on the frequency of the light while the intensity was determined by their number.

In 1905 Albert Einstein [16] explained the photoelectric effect in terms of a simple relationship

$$E_{kin,max} = \hbar\omega - \phi \qquad (2.2)$$

That is, the maximum kinetic energy E_{kin} of a photoemitted electron is equal to 'quantized package' of light energy related to the classical frequency ω minus the work necessary to release the electron from the emitter, the workfunction ϕ. This relationship contained two fundamental and novel assumptions viz, the photon or particle nature of light and the quantized nature of matter. In the excitation process it is assumed that the incident photon is absorbed by a single electron.

The photoelectric effect for metals may be subdivided into volume photoelectric effect and surface photoelectric effect [17]. The volume photoelectric effect is due to the emission of the bound electrons in the solid. This effect is of little importance near threshold, but should not be neglected in general. The surface

photoelectric effect is due to the emission of the `free' electrons in the conduction band, while they are interacting with the surface barrier. Mitchell [18,19] developed a model to explain surface photoelectric effect. He assumed that the wavelength of the incident monochromatic wave is large compared to the de-Broglie wavelength of the electrons in the conduction band. He also assumed that electrons moved in a Sommerfeld type of potential and the energy distribution of the electrons was given by Fermi-Dirac statistics.

One of the first explanations of photoemission, based on phenomenological models of the interaction of light with electron in a metal was developed by Fowler [20]. This is one of the first applications of quantum mechanics to solid state physics. Fowler derived an equation for the specific photoelectric emission from a metal surface as a function of the frequency of the incident light and temperature of the surface. Moreover Fowler has devised an ingenious graphical method of testing the theory and has shown that it is in excellent agreement with the best experimental results available at that time.

Immediately after the publication of the results of Fowler, Dubridge [21] suggested some modifications to Fowlers graphical method. By this method it became possible to determine the true photoelectric threshold of a surface

from photocurrent - temperature curves taken at a single incidence frequency and Dubridge's modification of Fowler's theory found to be more successful.

Works of Lawrence and Linford [10] on the effect of intense electric fields on the photoelectric properties of metals gave a greater insight into the phenomena. Shifts of photoelectric thresholds by strong accelerating fields are of particular interest for they involve changes of the workfunction of a surface without alteration of the important characteristics of the metal. The workfunction involves more than just the work required to eject an electron from inside to immediately outside a metal, since it also includes the work required to remove it entirely away from the surface. Outside the metal, an electron experiences a force of attraction produced by its image [22]. In some cases ion layers also produce electrostatic fields near metal surfaces, which oppose or aid the removal of electrons. Surfaces reduce the ion image fields, thereby causing the reduction of the workfunction. The lowering of workfunction appear as a shift of the photoelectric threshold to the red. Variation of the thermionic emission with applied fields have been used to estimate surface electric fields.

Kane [23] proposed a theory of photoelectric

emission from semiconductors. In his work he has determined the photoelectron yield versus energy relation for a number of possible photoelectric production and escape mechanisms involving volume and surface states in matter.

Assuming bulk photoemission from a solid, Berglund and Spicer [24] derived expressions for the quantum yield and for energy distribution of photoelectrons. The deduced expressions relate optical transition probabilities, optical constants, and mean free paths for inelastic scattering in a solid to quantities which can be measured in photoemission experiments.

Understanding of the physics of photoemission process provides an extremely sensitive method for detailed analysis of the electronic properties of atoms, molecules, condensed matter, surface properties etc.[25]. An important aspect of photoemission is its surface sensitivity, that is features of the emitted electrons like velocity, density, spectral features etc. are related to the properties of solid as defined by the outermost layers of atoms in the emitter. Hence, photoemission is intrinsically influenced by surface conditions and external parameters such as photon energy, angle/region of incidence, applied voltage etc.

2.2. Laser induced Photoemission from Metal Surfaces

Using high energy density laser beams it is possible to generate short intense and bright electron beams [26-30]. The time dependence of electron beams by other methods is dictated by the temporal characterization of their pulsed voltage sources. But using lasers with very high photon fluxes and nano second or pico second pulse rise times, it is possible to create electron beams of very short duration [31]. Such electron beams have many applications like transforming electron beam energy into the radiative field of a Free Electron Laser, microwave tube, synchrotron source etc.[6,9,29,32].

2.3. Multiphoton Photemission from Metals induced by ultra short Laser Pulses

Extensive use of lasers in various branches of experimental physics began in the sixties and has opened up opportunities to solve a number of fundamental problems. Among such applications, many-photon process in solids and particularly the photoelectric emission is of considerable interest.

Earlier works [33-36], explained laser induced emission current from different targets as only due

to thermal contributions. Conductors, semiconductors, and insulators were used as solid targets in these studies. It is observed that for different elements relative intensities appear to depend on the workfunction of the surface and on the ionization potential of the species in question. But the work carried out by David Lichtman and Ready [34] has investigated and shown the possibility of multiphoton induced photoemission. However,they also came to the conclusion that the emission is due to thermionic emission and could be described by Richardson equation.

But, Verber and Adelman [35] found it difficult to explain short signals aroused during laser irradiation unlike the case when the long signals were confirmed as thermionic. Adawi [37] and Smith [38] predicted a dependence of two photon photoelectric current on the direction of polarization of the beam. The first report of a photoelectric emission proportional to the square of the light intensity was that by Teich *et al* [39]. Farkas *et al* [40] proposed an effective model which made it possible to study photoelectric emission as a result of the absorption of three or more photons. The experiments were in good agreement with the theoretical calculation of the probability of the many photon photoelectric emission carried out by Adawi and Smith.

Measurements of the absolute values of the quantum efficiency of the two and three photon process also confirmed the qualitative correctness of the theoretical calculations [41]. Ready [42] was the first to study electron emission from metals using a Q-switched Ruby Laser. He was able to consider the details of the electron process.

There are certain characteristic features which distinguish photoelectric emission from thermionic emission. In contrast to the thermionic emission current, the photoemission current is proportional to the n^{th} power of the light intensity [43].

$$J_n = \eta_n I^n \qquad (2.3)$$

where η_n is the probability of n - photon effect. The order of the photoelectric effect can be deduced from the experimental data and compared with theoretical value [44]

$$n = 1 + \frac{A}{\hbar\omega} \qquad (2.4)$$

where A is work function for emission from a metal. The agreement between the value of `n´ and that found experimentally can be regarded as an important evidence in support of the photoelectric nature of the measured current.

Since in the photoelectric effect, the emission of electrons as a result of the incidence of photons on the cathode is an instantaneous process, the current pulse shows a delay relative to the laser pulse.

In the Guassian profile of the laser pulse the duration 't_j' of the photocurrent pulse is related to the laser pulse duration 't_o' by [44]

$$t_j = \frac{t_0}{\sqrt{n}} \qquad (2.5)$$

In thermionic emission case the shape of a current pulse is governed by the time dependence of the target temperature.

Thermionic emission current is governed entirely by the temperature of metal surface, which in turn depends on the absorbed power. While, photoelectric current is governed by the electric vector of the incident wave and thus on the angle of incidence and on the angle of polarization of light [45-47]. Thus measurements of the angular and polarization dependence of the emission current make it possible to distinguish the many photon photoelectric effect.

Photoemission from metal cathodes is explained theoretically in two ways; pure multiple-photon photo emission and multiple-photoemission combined with thermal emission.

2.3.(a). Multi-photon photoemission from metals without heating

Multiple photon photoemission from a metal surface at a temperature $T = 0^{o}$ K, is considered. The calculations of pure multiple photon photoemission have been either for the so called surface photoemission effect or for the volume photoelectric effect. The initial calculations for the two photon surface photoemission effect were done by Adawi [37] and Smith [38]. Calculations of higher order multiple-photon effects have been given by Bunkin and Federov [47] and by Silin [48].

A theoretical treatment of two photon volume photoemissive effect was first given by Bloch [48]. Bloch's calculation has been criticized by Teich and Wolga [50], who observed that Bloch failed to account for the following:

(i) the electron escape depth is a function of electron energy

(ii) part of the incident light is reflected at the surface

(iii)the perturbation Hamiltonian in the independent electron scheme is

$$H = \frac{-eA.P}{mc} + \frac{e^2 A^2}{2mc^2} \quad (2.6)$$

and two photon transition may occur either from the first term in second order or from the second term in the first order. Bloch neglected the first term. Teich and Wolga [50] obtained an explicit relation for the two photon photoemission current and found that their calculation was in good agreement with their experimental result.

Logothetis and Hartman [41] used a similar multiquantum volume photoemission model to explain their experiments on gold. As it is deduced for two-photoemission, two-photon induced current density J_2 is given by

$$J_2 = \frac{ep\, I^2 (1 - R)^2 \beta p\bullet}{h\nu\, (2\alpha + 1/l)} \quad (2.7)$$

e - the electron charge,p - the electron escape probability, R - the metal reflectivity, I - the incident power per unit area, $h\nu$ - the incident photon energy, α - the absorption coefficient at the laser wavelength, l -

electron escape depth and β_{pe} - is the two photon absorption coefficient that results in photoemission transition.

2.3.(b). Multiple-photon photoemission combined with thermal emission mechanism

The Generalized Fowler - Dubridge theory

The first successful theory to explain both the temperature dependence of one-photon photoemission and the spectral dependence of one-photoemission near the work function threshold was developed by Fowler [18]. Fowler's starting point is the assumption that the electron in the metal obey Fermi-Dirac statistics and are uniformly distributed in the momentum space. He calculated the one-photon quantum yield for three different models that depended on how the photon was absorbed and how the electron escaped. Thereafter Dubridge [20,51] extended Fowler's calculations using slightly different assumption for, both the photon absorption and the electron emission, and he calculated the one-photon quantum yield as a function of temperature and one photon energy.

The ideas of Fowler and Dubridge can be extended to more general electron emission effect. The total electron emission current is composed of partial current densities

each of which has a simple interpretation. Thus the total current can be written as [52,53]

$$J(r,t) = \sum_{n=0}^{\infty} J_n(r,t) \qquad (2.8)$$

The quantity J_0 is interpreted as thermionic emission, J_1 as one-photon photoemission, J_2 as two-photon photoemission and J_n as n-photon induced photoemission. The functional form of the partial current density for n-photon photoemission can be written as

$$J_n(r,t) = a_n\left(\frac{e}{h}\right)^n A\, I(r,t)^n\, (1-R)^n\, T(r,t)^2\, F\left(\frac{nh\nu - \phi}{kT}\right) \qquad (2.9)$$

e - the electron charge, R - the surface reflectivity, A - the theoretical Richardson coefficient, $h\nu$ - the laser photon energy, ϕ - the surface work function, k - Boltzmann's constant, I - the the incident laser irradiance, T - the absolute temperature of the surface and a_n - a constant. F(x) is the Fowler function.

A comparison of (2.7) and (2.9) shows that

the constant a_2 can be related to the escape probability p, the two-photon absorption coefficient

$$a_2 = \frac{p\,\beta_{pe}\,h^4\,\nu}{2\,\pi\,m\,e^2\,(\,2\alpha + 1/l\,)\,(2h\nu - \phi\,)^2} \qquad (2.10)$$

The constant a_2 can also be related to the measured emitted charge q, if the electron emission is a pure two-photon effect. In this interpretation a_2 is a completely empirical parameter and is found by choosing a_2 such that the measured charge is equal to the theoretical expression for the emitted charge,

$$q = \int J(r,t)\,.\,ds\,dt \qquad (2.11)$$

The integration is to be taken over the pulse duration and the pulse area. The total current density J (r,t) is given by equation (2.8) if both the space-time dependence of the incident laser irradiance and the surface temperature are known. The irradiance usually known from the experimentally measured laser diagnostics, but the surface temperature as a function of space and time must be calculated from the heat conduction equation

$$\nabla^2 T(r,t) - \frac{1}{k}\,\frac{\partial T\,(r,t)}{\partial t} = -\,\frac{G\,(r,t)}{K} \qquad (2.12)$$

k - the thermal diffusivity, K - the thermal conductivity and G(r,t) - the net energy generated per unit volume per unit time within the metal.

2.4. Photoemission Optogalvanic Spetroscopy

Photoemission Optogalvanic (POG) effect is as explained earlier the production of optogalvanic signals by injecting electrons into a discharge via photoelectric effect [54-58]. Because of the pumping of electrons, an avalanche develops in the discharge,which yields a considerable increase of the plasma current which constitutes the POG signal.Because the magnitude of the signal produced by a laser incident on an electrode is affected by the surface composition, this method is a useful and appropriate analytical tool. When the electrode is being etched, changes in surface composition affect the photoemission yield. Physically, the workfunction or carrier mobility of the electrode surface changes during the etch and the photoemission efficiency varies for a given photon energy and flux. By changing the photon energy and/or flux, the technique can be tailored to measure plasma etching end points or surface contamination. Besides this, the understanding of POG is strongly related to that of rf and other nonstationary discharges. In some respects the POG effect is the response of the discharge to an instantaneous

perturbation and its observation yields directly the relevant time scales. In addition, the analysis of the time dependence of the observed POG signals may give some information about the secondary-electron -emission coefficient by ion impact on the cathode.

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