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Plasmon energy of semiconductors

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***Abstract*— Plasmon energy is estimated quantitatively from electronegativity and principal quantum number of constituent atoms of binary semiconductors and ternary chalcopyrite semiconductors. It is based on the basis of structure property relationship in solid state sciences. The estimated values of Plasmon energy are in good agreement with the reported values in literature .In these semiconductors crystal chemical factors such as electronegativity and principal quantum number delineates the chemical bonding behaviour of constituent atoms of the compounds.**

***Index Terms*— Plasmon energy, Electronegativity, Principal quantum number.**

I. INTRODUCTION

Numerous attempts have been made to derive an empirical relationship between Plasmon energy and various physical parameters of binary and mixed semiconductors [1-10]. The compound and ternary chalcopyrite semiconductors have received much attention because of their potential application in the field of light emitting diodes, nonlinear optics, photovoltaic devices and solar cells. Similar attempts at empirical correlation between Plasmon energy and crystal parameters have been more successful [11-13]. Several investigators have demonstrated empirical correlation between Plasmon energy with bulk modulus and micro hardness [14], cohesive energy [15], heat of formation[16],dielectric constants[17-19], polarisability [20,21], and susceptibility [22] of semiconductors. Kumar et al [23] have used Plasmon oscillation theory of solids to evaluate the mechanical, optical and electrical properties of semiconductors using Plasmon energy as input parameters. Plasmon energies have been estimated by them using three input parameters as molecular weight, density and number of valence electrons taking part in collective oscillation. Reddy et al [24] has estimated Plasmon energy of semiconductors and alkali halides using the interatomic distance of compounds. Considering the above empirical concept an alternative method has been adopted for the estimation of Plasmon energy of tetrahedral semiconductors using electronegativity of constituent atoms and average principal quantum number of atoms constituting the compounds.

II. THEORY

The quantised energy of collective oscillation [1, 2] of valence electron is known as Plasmon. Plasmon's are also known as quasiparticles. These collective oscillation in which valence or conduction electron participate are a consequence of inertia of the electrons and of theirs repulsive coulomb interaction. Such longitudinal plasma oscillations in a solid can be excited in the electron gas either by fast energetic bombarding electrons [3] or during X ray and auger electron transition [4]. Experimentally to understand these quantised energy of collective oscillation of valence electrons, scientist used electron energy loss spectroscopy (EELS), which have been reported recent years [14, 16]. Plasmon energies even through a direct method of calculation from the effective number of valence electrons taking part in plasma oscillation is available in literature **[**7].The valence electron plasma energy, $\hbar\omega_p$,given by Jackson [1] is as follows:

$$\hbar\omega_p = 28.8\left(\frac{Z\rho}{M}\right)^{\frac{1}{2}} \quad (1)$$

where Z is the total number of valence electron, ρ is the density (gmcm^{-3}) and M is the molecular wt.(gm) of a solid..The Fermi energy is also evaluated from the relation as follows

$$E_F = 0.2947(\hbar\omega_P)^{\frac{4}{3}} \quad (2)$$

Reddy et al [24] has shown the dependence of valence electron Plasmon energy on interionic distance of compound semiconductors and alkali halides .The equations are as follows

$$\hbar\omega_p = -a_1(r_0) + b_1 \quad (3)$$

where $\hbar\omega_p$ and r_0 are the valence electron plasma energy(eV) and interionic distance(A^0) respectively. The numerical values of a_1 and b_1 are 6.78, 34.44, 8.99, 37.80 and 8.08, 39.10 for II-VI, III-V group semiconductors and alkali halides respectively. Koh et al [30] found a suitable relationship between Plasmon energy with an ionic ratio in II-VI and III-V Semiconductors**.** Reddy et al [28] have proposed an empirical relation between elastic constants C_{44} with the lattice energy as follows

$$U = m_3 C_{44} + b_3 \quad (4)$$

where m_3 are slopes and b_3 are intercepts for compound semiconductors respectively, which are obtained by using least square method .Kumar et al [20] have studied the quadratic relation between lattice energy U and plasma energy ($\hbar\omega_p$) as

$$U = k_1 + k_2(\hbar\omega_p) - k_3(\hbar\omega_p)^2 \quad (5)$$

where k_1 =421.22, k_2 =27.94 and k_3 =0.178, combining equation (4) and equation (5) the following relation between elastic constants C_{44} and plasma frequency ($\hbar\omega_p$) is expressed below as

$$C_{44} = \frac{1}{m_3}[(k_1 - b_1) + k_2(\hbar\omega_p) - k_3(\hbar\omega_p)^2 \quad (6)$$

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using the values of k_1, k_2, k_3 and m_3 and b_3 from [28,29], one can evaluate plasma energy of the compounds. Reddy et al [27] has proposed an empirical relation between Plasmon energy and electronegativity difference (ΔX^*) of alkali halides as follows

$$\hbar\omega_p = A(\Delta X^*) + B \qquad (7)$$

where A and B are constants and their numerical values are A =3.59 and B =5.91 respectively. The valence electron Plasmon energy can also be calculated from the refractive index of the material using an empirical relationship **[**25**]**

$$\hbar\omega_p = k_1 e^{-k_2 n} \qquad (8)$$

where the numerical value of constants k_1 and k_2 are 22.079,0.1779 and 47.924,0.3546 for II-VI and III-V group semiconductors. This relation has been successfully applied to predict their Plasmon energies even through a direct method of calculation from the effective number of valence electrons taking part in plasma oscillation in available in literature **[**1-3].During the interaction between high energy electron beam with the outermost valence electrons in an atom constituting compounds, the following things may happen

(i) Every Crystals have definite structure which is related to bond energy. This bond energy is responsible for the formation of structure of solids. The bond energy comes from a perfect sharing of valence electrons which may be assumed to be a function of electronegativity of both the atoms. All bonding is a consequence of the electrostatic interaction between nuclei and electrons obeying Schrödinger equation. Ionic bonding is caused by the electrostatic attraction between positively and negatively charged ions (usually non-metal atom and metal atoms).The ions are produced by a transfer of electrons between two atoms with a large difference of electronegativity, the electronegativity of atoms is the tendency of an atom to attract electron towards itself when chemically combined with another element.

(ii) When the cation and anion approach each other close enough that electrons orbital in the ions begin to overlap ,the valence electrons begin to repel each other because of the repulsive electrostatic force ,of course the closer together the ions are ,the greater the repulsive force. The Pauli Exclusion Principle also plays an important role in the repulsive force.

The present study is based on the above explanation and analysis it is proposed an empirical approach on the basis of chemical bond theory for the estimation of Plasmon energy of tetrahedral semiconductors .For an individual bond, the Plasmon energy contribution can be separated into ionic and covalent parts. In ionic crystal Vander wall interaction are neglected because of their relatively small contribution to the Plasmon energy. As there is no pure ionic bonding in crystals so cation cannot completely lose all its valence electrons. It is assumed that Plasmon energies of a crystal can be separated into ionic and covalent part, the ionic contribution to the crystal lattice comes from electrostatic attraction and repulsive interaction of the ion pairs, and the covalent contribution arises from overlap of electron cloud.It is correlated Plasmon energy with electronegativity of atoms constituting compounds and average principal quantum number of atoms in compounds. The homopolar energy gap is related to bond length and bond length is related to Plasmon energy. The larger the principal quantum number, the longer the distance between nuclei and valence electrons, the distortion of outer electronic shell is reflected by principal quantum number which is related to bond length and ultimately to Plasmon energy, other factor the ionic part, the heteropolar part is reflected by electronegativity value of all atoms, the attractive power of effective nuclear charge to valence electrons in outer orbital's is related to Plasmon energy. For binary tetrahedral semiconductors of II-VI and III-V type Plasmon energy is empirically related to $\frac{\eta_{av}}{(\chi_A\chi_B)^{1/2}}$, where $\eta_{av} = \frac{\eta_A + \eta_B}{2}$ is the average principal quantum number of valence electrons of atoms A and B. χ_A and χ_B are electronegativity values of A and B atoms respectively. For II-VI and III-V semiconductors the Plasmon energy is estimated by the following empirical relation as

$$\hbar\omega_P = M * \left(\frac{\eta_{av}}{(\chi_A\chi_B)^{1/2}} \right) + N \qquad (9)$$

where M and N are constants and depends on crystal structure. Their numerical values are -4.8736, 28.112 and 4.1097, 27.986 for II-VI and III-V semiconductors respectively. The Plasmon energy of ternary chalcopyrite semiconductors ABC_2 consist of three contribution of atoms A, B and C .The overall effect of electronegativity of both cations A and B and the effects of electronegativity of two anions C on the Plasmon energy of the materials can be expressed as $(\chi_A\chi_B)^p$ and χ_c^{2q} and the Plasmon energy is linearly related as $\frac{\eta_{av}}{\left[(\chi_A\chi_B)^P \chi_C^{2q}\right]}$ where η_{av} is the average principal quantum number of the four constituent atoms in ABC_2 . $\eta_{av} = \left(\frac{\eta_A + \eta_B + 2\eta_C}{4} \right)$ and $p = 1/4$ and $q = 1$. A graph is plotted between Plasmon energy as a function of electronegativity and average principal quantum number of all atoms in the compounds in Fig.1-2 for all crystals. On the basis of least square fitting and calculation, the trend lines, the correlation equations between Plasmon energy and electroneagtivity and average principal quantum number and the value of squares of correlation coefficient $R^2$are given in Fig.1-2. The correlated equation and the squares of the correlation coefficient R^2, which can be used to measure the effectiveness of the least square fitting, are also shown in the plotted figure). From figure1-2 ,it is seen that Plasmon energy and electronegativity and average principal quantum number are linearly related,R^2 value are greater than 0.78 for ternary chalcopyrite and 0.8057 for binary semiconductors. Therefore, the effectiveness of least square fittings is reliable and normal mathematical expression between Plasmon energy and electronegativity and average principal quantum number for ABC_2 chalcopyrite semiconductors are as follows

$$\hbar\omega_p = \frac{R\eta_{av}}{[(\chi_A\chi_B)^{\frac{1}{4}}\chi_C{}^2]} - S \qquad (10)$$

where R and S are constants and their numerical values are -5.3669,20.139 and -3.7138,18.44 for II-IV-V and I-III-VI chalcopyrite semiconductor respectively. From empirically obtained equations and the correlations between Plasmon energy with average principal quantum number and electronegativity of each atom constituting compounds can be expressed as

$$\hbar\omega_p = f\left(\chi_i,\ \eta_{av}\right) \qquad (11)$$

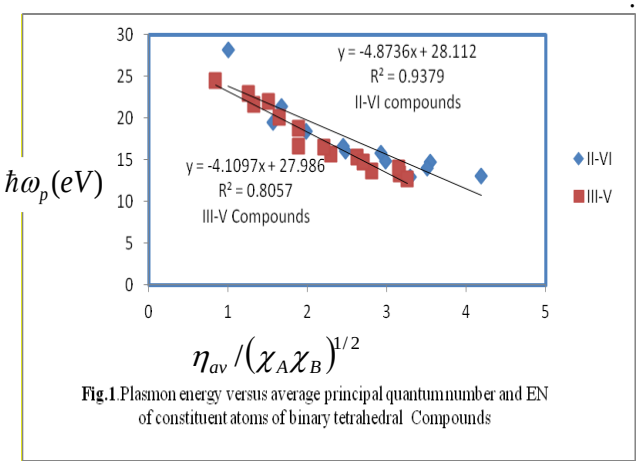

Fig.1 Plasmon energy versus average principal quantum number and EN of constituent atoms of binary tetrahedral Compounds

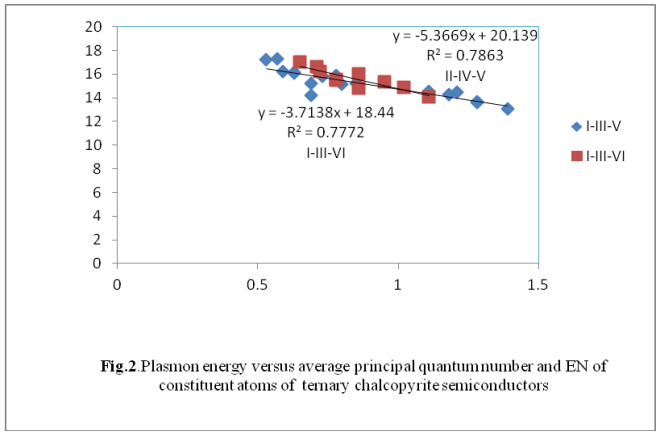

Fig.2 Plasmon energy versus average principal quantum number and EN of constituent atoms of ternary chalcopyrite semiconductors

Table 1
Calculated and previously reported values of Plasmon energy of binary tetrahedral semiconductors.

Crystals	$\eta_{av}/(\chi_A\chi_B)^{1/2}$	$\hbar\omega_p$ (eV) Calculated Eqn.(9)	$\hbar\omega_p$ (eV) Reported values	
			V .Kumar Ref.[14]	Reddy Ref.[24]
BeO	1.00	23.88	28.26	-
BeS	1.57	21.53	19.52	-
BeSe	1.98	19.85	18.39	-
BeTe	2.48	17.79	16.12	-
ZnO	1.67	21.12	21.48	-
ZnS	2.45	17.92	16.71	18.44
ZnSe	2.93	15.94	15.78	17.83
ZnTe	3.55	13.4	14.76	16.61
CdS	2.98	15.74	14.88	14.57
CdSe	3.51	13.56	14.01	14.03
CdTe	4.19	10.77	13.09	-
MgTe	3.26	14.47	12.97	-
HgS	3.35	14.22	14.85	-
HgSe	3.90	11.96	13.99	-
HgTe	4.61	9.04	12.85	-
BN	0.84	23.88	24.75	26.29
BP	1.32	21.53	21.71	-
BAs	1.64	19.85	20.12	-
AlN	1.26	17.79	22.97	21.08
AlP	1.89	21.12	16.65	16.67
AlAs	2.29	17.92	15.75	15.95
AlSb	2.81	15.94	13.72	13.91
GaN	1.51	13.4	21.98	-
GaP	2.21	15.74	16.50	16.58
GaAs	2.62	13.56	15.35	15.95
GaSb	3.16	10.77	13.38	13.98
InN	1.89	14.47	18.82	-
InP	2.70	14.22	14.76	14.97
InAs	3.15	11.96	14.07	14.25
InSb	3.76	9.04	12.73	12.63
TiN	1.54	21.65	-	-
TiP	2.25	18.73	-	-
TiAs	2.66	17.05	-	-
TiSb	3.21	14.79	-	-

Table 2
Calculated and previously reported values of Plasmon energy of ternary chalcopyrite semiconductors

Crystals	$\eta_{av}/\left[(\chi_A\chi_B)^{1/4}\chi_C^2\right]$	$\hbar\omega_p$ (eV) Calculated Eqn.(10)	V.Kumar Ref. [16]
$CuAlS_2$	0.53	16.67	17.25
$CuAlSe_2$	0.73	15.89	15.86
$CuAlTe_2$	1.11	14.4	14.35
$CuGaS_2$	0.57	16.52	17.10
$CuGaSe_2$	0.78	15.69	15.92
$CuGaTe_2$	1.18	14.12	14.30
$CuInS_2$	0.63	16.28	16.12
$CuInSe_2$	0.86	15.38	15.09
$CuInTe_2$	1.28	13.73	13.66
$AgAlS_2$	0.59	16.44	16.26
$AgAlSe_2$	0.80	15.61	15.16
$AgAlTe_2$	1.21	14	14.50
$AgGaS_2$	0.63	16.28	16.10
$AgGaSe_2$	0.85	15.42	14.76
$AgGaTe_2$	1.28	13.73	13.63
$AgInS_2$	0.69	16.05	15.21
$AgInSe_2$	0.93	16.05	14.23
$AgInTe_2$	1.39	13.3	13.04
$ZnSiP_2$	0.65	16.2	17.02
$ZnGeP_2$	0.71	15.97	16.64
$ZnSnP_2$	0.78	15.69	15.55
$ZnSiAs_2$	0.86	15.38	16.05
$ZnGeAs_2$	0.93	15.1	15.66
$ZnSnAs_2$	1.02	14.75	14.82
$CdSiP_2$	0.72	15.93	16.19
$CdGeP_2$	0.78	15.69	15.52
$CdSnP_2$	0.86	15.38	14.82
$CdSiAs_2$	0.95	15.02	15.53
$CdGeAs_2$	1.02	14.75	14.90
$CdSnAs_2$	1.11	14.4	14.12

III. RESULTS AND DISCUSSION

Plasmon energy of semiconductors(binary and ternary chalcopyrite semiconductors) is estimated using equation (9) and equation (10).The estimated values are given in Table 1 and Table 2 along with the results of earlier researchers

[14,16,24] for comparison. It is evident that the calculated values are in better agreement with previous researchers [23-29].The proposed empirical relation helps to estimate Plasmon energy of binary and ternary semiconductors in terms of electronegativity value and average principal quantum number of valence electrons because inclusion of electronegativity and principal quantum number has some bearing on the concept of chemical bonding. The difference of electronegativity value of cation and anion of compounds has not being taken, electronegativity of each atom has been considered. Instead of using molecular weight, specific gravity and number of valence electrons [8], only two parameters, average principal quantum number and electronegativity of each atoms in the compound has been considered. This is very simple and the calculation can be done with the help of calculator. No experimental data is required in this case. Moreover these two parameters electronegativity and average principal quantum number delineates the structure property relationship in solid state sciences. Plasmons result from the collective excitation of the valence electrons and also reflect the solid state character of the compounds. In this model one can calculate the values of Plasmon energy of these compounds without any knowledge of experimental data except electronegativity of each atom and average principal quantum number of valence electron. However previous model requires specific gravity ,molecular weight and number of valence electron.[14] and interionic distance of compounds.[24].Therefore we claim that this would be a better approach to estimate Plasmon energy(empirically) of semiconductors and other compounds as well.

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