This material may be protected by Copyright law (Title 17 U.S. Code)

Eur. Phys. J. Appl. Phys. (2012) 58: 30201
DOI: 10.1051/epjap/2012120062

THE EUROPEAN PHYSICAL JOURNAL
APPLIED PHYSICS

Regular Article

Electrical and optical properties of an organic semiconductor metal-free phthalocyanine ($C_{32}H_{18}N_8$)

M.E. Azim-Araghi[1,a], J. Baedi[2], and L. Moazzami Goodarzi[1]

[1] Physics Department, Tarbiat Moallem University, 49 Mofateh avenue, Tehran, Iran
[2] Physics Department, University of Sabzevar Tarbiat Moallem, Sabzevar, Iran

Received: 16 February 2012 / Received in final form: 21 April 2012 / Accepted: 9 May 2012
Published online: 5 July 2012 – © EDP Sciences 2012

Abstract. In a recent work we calculated some electronic properties of metal-free phthalocyanine such as band structure, density of states and energy gap. We have also presented some optical properties such as dielectric function, electrical loss function, optical conduction, absorption and refractive index, some of which have never been studied before. Calculations were performed in the framework of density functional theory (DFT), using the full-potential linearized augmented plane wave (FP-LAPW) method. This study presents the electrical gap energy of metal-free phthalocyanine to be $E_g = 2.4$ eV which is in good agreement with experimental data. A trap energy level is also observed. Optical band gap is about 2.48 eV with an optical trap level at 1.48 eV. In addition, we obtained the static refractive index in the x-, y- and z-directions as $n_{0xx} = 2.43$, $n_{0yy} = 2.06$ and $n_{0zz} = 2.32$. Finally, absorption spectra display the existence of strong absorption bands at the wavelengths of 400 and 800 nm which compare favorably with experimental results.

1 Introduction

Metal-free phthalocyanine (H_2Pc) was first discovered in 1907 by Braun and Tcherniac and in 1930 the molecular structures of H_2Pc and metal Pcs (MPcs) were found and confirmed. Pcs form a large group of organic semiconductor compounds, which have been the main basis for the search of molecular semiconductors. They have a porphyrin-like structure in which the *aza*-bridge carbons are substituted by nitrogens, surrounded by four benzene rings and two hydrogens are located in the center of the macrocycles. The most interesting derivative is a dianion that may be complexed with up to 70 different metal cations which determine the electronic, optical and magnetic properties [1–3]. H_2Pc has two polymorphs (or crystalline forms), the α- and β-forms. The β-form is more thermodynamically stable than the α-form. The α-form can be converted into the β-form by heating the solid material under vacuum for a time long enough depending on the temperature used for the conversion [4]. So in the present work, the structural properties of β-form were studied. Pcs have many attractive properties such as availability in high purity due to the ease of crystallization and sublimation, extraordinary thermal and chemical stability. Also intense absorption is noticed in the red and blue spectrum range, which makes them very pure blue pigments [2,5]. Because of these distinctive characteristics, Pcs have been widely used as pigments for coloring plastics and metal surfaces, and as catalysts in the oil industry [5]. In recent years, new applications have emerged for Pcs due to their semiconducting properties. They have been used in photovoltaic devices, photodetectors, photoresistive detectors, organic transistors and solar cells. Moreover, they are promising candidates for optical and electronic devices for gas sensing sensors because of their electronic properties [3–13]. Pcs are also commonly used as a hole injection layer in organic light-emitting diodes (OLEDs) [14,15]. The knowledge of the electrical and optical properties is necessary to understand the fundamental aspects of the materials. Therefore, the aim of the present work is to investigate and analyze these properties of metal-free phthalocyanine to confirm some essential parameters and predict more optical properties.

2 Method of calculations

The calculations were performed in the framework of density functional theory (DFT) [16], using the full-potential linearized augmented plane wave (FP-LAPW) method as implemented in Wien2k codes [17,18]. We selected the generalized gradient approximation (GGA) of Kronig for the exchange correlation energy in our calculations [19]. The chosen radii of MT spheres for atoms are RMT $(C) = 1.16$ Å, RMT $(N) = 1.13$ Å and RMT$(H) = 0.61$ Å. The separation energy, which defines the separation into core

[a] e-mail: azim@saba.tmu.ac.ir

Samsung Exhibit 1037, Page 1 of 6

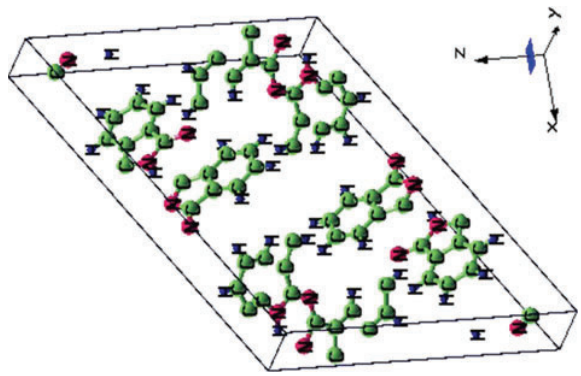


Fig. 1. (Color online) Structure and atomic positions of metal free phthalocyanine ($C_{32}H_{18}N_8$).

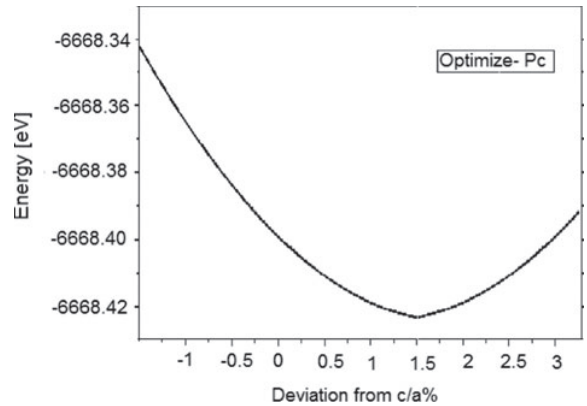


Fig. 2. Changes of energy ratio to different values of c/a%.

and band states, was chosen to be about −6.0 Ryd. Figure 1 pictures the crystal unit cell of H_2Pc, it has a monoclinic structure with P21/a space group in which there are two phthalocyanine molecules per unit cell.

Dielectric tensor is used for analyzing the behavior of crystal before the electromagnetic field. The real part of this function is indicated with $\varepsilon_1(\omega)$, and the imaginary part with $\varepsilon_2(\omega)$, so we have:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + \mathrm{i}\varepsilon_2(\omega). \tag{1}$$

We applied Kramers-Kronig transformation to analyze the data. This transformation allows us to calculate the real part of the dielectric function when having its imaginary part. The imaginary and real parts of the dielectric constant at the frequency of the incident photon can be written as [20]:

$$\mathrm{Im}\varepsilon_{ij} = \frac{4\pi e^2}{m^2\omega^2} \times \sum_{c,v} \int \mathrm{d}k \langle c_k|p^i|v_k\rangle\langle v_k|p^j|c_k\rangle \times \delta(\varepsilon_{ck} - \varepsilon_{vk} - \omega), \tag{2}$$

$$\mathrm{Re}\varepsilon_{ij}(\omega) = \sigma_{ij} + \frac{2}{\pi} p \int_0^\infty \frac{\omega' \mathrm{Im}\varepsilon_{ij}(\omega')}{\omega'^2 - \omega^2} \mathrm{d}\omega', \tag{3}$$

where $|c_k\rangle$ and $|v_k\rangle$ are conduction and valence states of the electron in a given wave vector k, and the delta function implies the conserving of the energy in transitions, where ε_{ck} and ε_{vk} are energies of the scattered electron in the initial valence and final conduction states, respectively. Two factors are effective for determining optical properties, density of states (DOS) above the Fermi level and the number of crystal symmetries which are discussed in the following sections.

3 Results and discussion

At first, we determine new lattice parameters by volume optimization ratio to energy. This volume optimization is calculated with the alteration to the rate of c/a. As illustrated in Figure 2 the minimum value of energy for this crystal occurs at 1.5%. The values of lattice parameters are presented in Table 1.

Table 1. Comparing the lattice vector in GGA method with the experimental method.

Method	a (bohr)	b (bohr)	c (bohr)
GGA (this work)	37.15	8.84	28.24
Experimental [21]	37.398	8.9	27.88

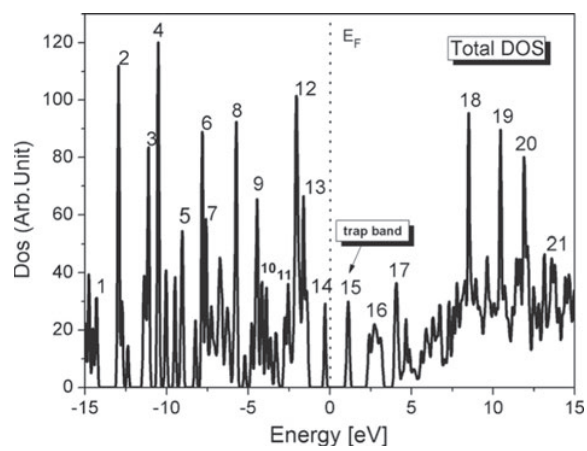


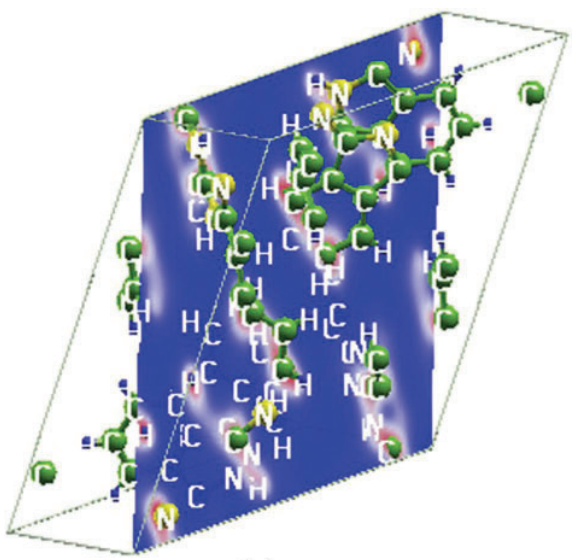
Fig. 3. Total DOS of metal-free phthalocyanine ($C_{32}H_{18}N_8$).

The total density of states (DOS) is exhibited in Figure 3 (attached detail is given in Tab. 2). Zero energy marks the Fermi level and is shown by the dashed line. The major contribution at the top of the valence band belongs to nitrogen atoms, which is due to their stronger electronegativity than carbon atoms in carbon-nitrogen bond (peaks of 11, 12 and 13). In addition, the peaks of 3, 5, 6 and 9 denote the overlapping of N-2P and C-2S orbitals. It should be noticed that there are two types of hybrid orbitals for carbon-carbon bond (peaks of 8, 14). The sp^2 orbitals are related to benzene rings and the other hybrid orbitals belong to the bonds between carbons which are out of the benzene rings. The conduction band mostly contains hybrid orbitals of carbon-nitrogen bonds. Also a trap

Samsung Exhibit 1037, Page 2 of 6

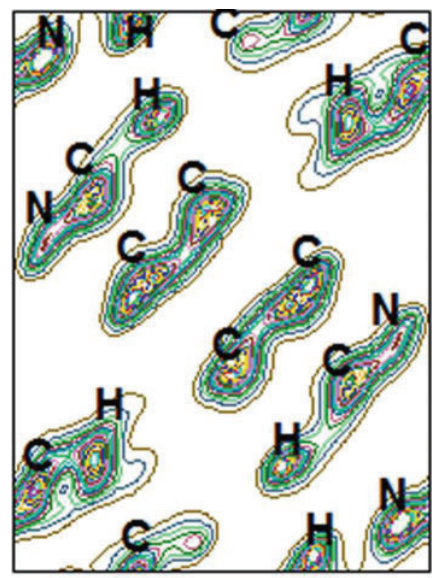
Table 2. The highest density of state related to different orbitals.

Peak number	Related to atom orbitals	Peak number	Related to atom orbitals	Peak number	Related to atom orbitals
1	C_{10}, C_{12}, C_{13}, N_3-2S	8	C_4, C_5, C_{10}, C_{12}, C_{13}, C_{16}-2P	15	C_1, C_8, C_9, C_{16}-2P N_1, N_2, N_3-2P
2	C_9-2S	9	C_2, ..., C_7, C_{12}, C_{13}, N_2-2P	16	C_{11}, C_{13}, C_{14}, N_1-2P
3	C-2P, N_2, N_4-2P	10	C_2, ..., C_7-2P, H_1, H_5-1S	17	C_4, C_5, C_6, C_9, C_{10}-2P, C_{12}, C_{13}, C_{14}-2P
4	N_3-2P	11	N_1, N_2, N_4-2P	18	C_1, C_3, ..., C_8, C_{10}, C_{12}, ..., C_{16}-2P N-2P
5	C_3, ..., C_9, C_{12}, C_{13}, C_{16}-2P N_2, N_3, N_4-2P	12	N_1-2P	19	C_1, C_2, C_8, C_9, C_{16}-2P
6	C_1, C_8, C_9, C_{13}, N_2-2P	13	N_2, N_4-2P	20	C_1, C_2, C_3, C_5, ..., C_{11}, C_{13}-2P N_1, N_4-2P
7	C_1, C_3, C_6, C_8, N_2, N_3-2P H_1, H_5, H_7, H_8-1S	14	C_1, C_8, C_9, C_{12}, C_{13}, C_{16}-2P	21	C_1, ..., C_{12}, C_{16}, N-2P



(a)

Fig. 4a. (Color online) Side view of (1 1 0) plate.



(b)

Fig. 4b. (Color online) Contours of electron charge density in the (1 1 0) plate.

band exists at the position of 15th peak [22]. The physical properties are controlled by traps, which are associated with dislocations, imperfections, grain boundaries [23]. It is remarkable that the contribution of H-1S orbital is the least because of its low electronegativity. Figure 4a represents the (1 1 0) plate and contours of the electric charge density are shown in Figure 4b. It is evident that apart from N-H bond which is a hydrogen bond, all other bonds are covalent.

The band structure related to the chosen point of Figure 5a is displayed in Figure 5b. It should be noted that the energies have been shifted so that the Fermi energy is located at the top of the valence band as zero energy. It is observed that this compound has an indirect band gap with an energy gap of about $E_g = 2.4$ eV which is in good agreement with the experimental value [24].

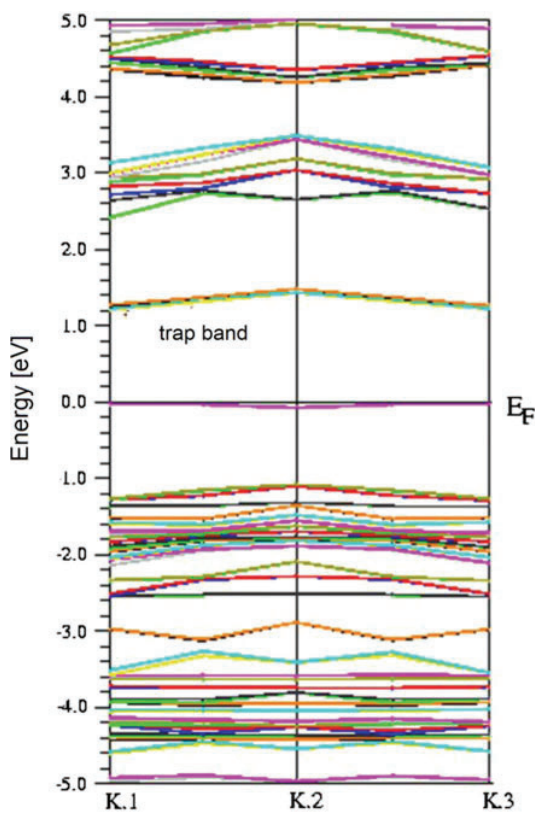
3.1 Optical properties

The real part of the dielectric functions for the x-, y- and z-directions is illustrated in Figure 6. As shown in the diagrams any of the directions has different value for dielectric function. The values related to $E = 1.32$ eV in x-, y- and z-directions are 14.29, 14.52 and 21.77 respectively. Indeed, there is anisotropy with the energies less than 5 eV because of no accordance between diagrams in all three directions.

Samsung Exhibit 1037, Page 3 of 6

(a)

Fig. 5a. (Color online) First Brillouin zone (K.1, K.2, K.3 are the chosen points).



(b)

Fig. 5b. (Color online) Band structure of metal-free phthalocyanine compound along the lines with high symmetry. The Fermi energy has been set to zero.

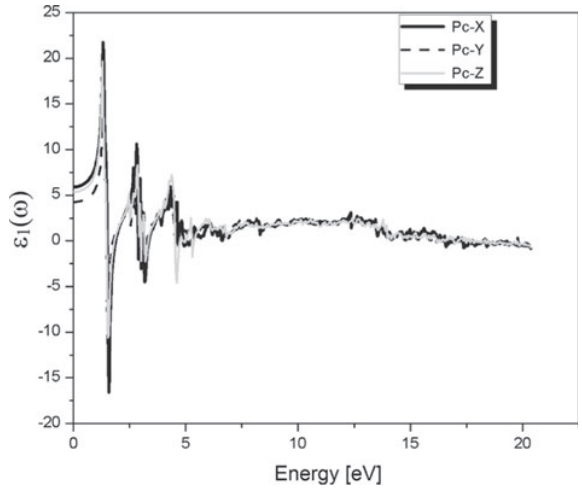


Fig. 6. Real part of the dielectric function of metal-free phthalocyanine.

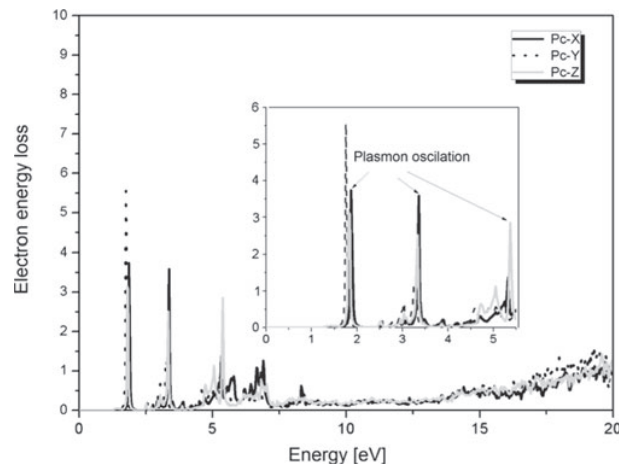


Fig. 7. Energy loss function of metal-free phthalocyanine (H_2Pc).

Roots of the real part of the dielectric function are a necessary condition for plasmon oscillations, but are not enough. We must also study the energy loss function for exact determination [25].

Figure 7 shows the energy loss function in all three directions. The maximum values of energy loss function in x-direction are at energies of 5.32, 3.36 and 1.89 eV which are in good agreement with the roots of Figure 5b at energies of 5.21, 3.36 and 1.89 eV. Therefore, this compound has three plasmon oscillations.

In Figures 8 and 9, energies related to maximums in the imaginary part of dielectric function and optical conduction are the same. So we just analyze optical conduction since analyzing the imaginary part of dielectric function results is nothing new.

The electrons of occupied states are excited to unoccupied states above the Fermi level by the absorption of photon energy. This is called optical conduction, which is the same in all three directions. Threshold

Samsung Exhibit 1037, Page 4 of 6

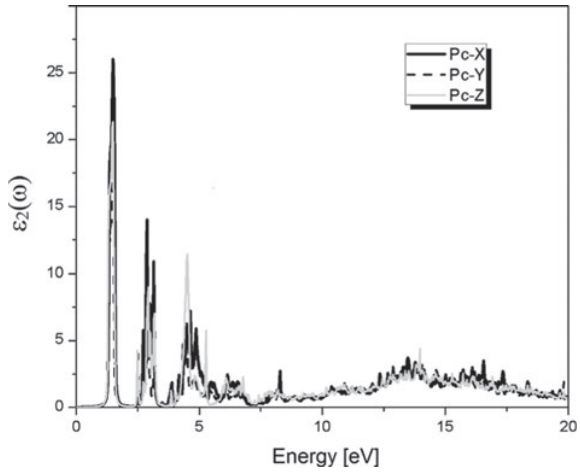


Fig. 8. Imaginary part of the dielectric function of metal-free phthalocyanine.

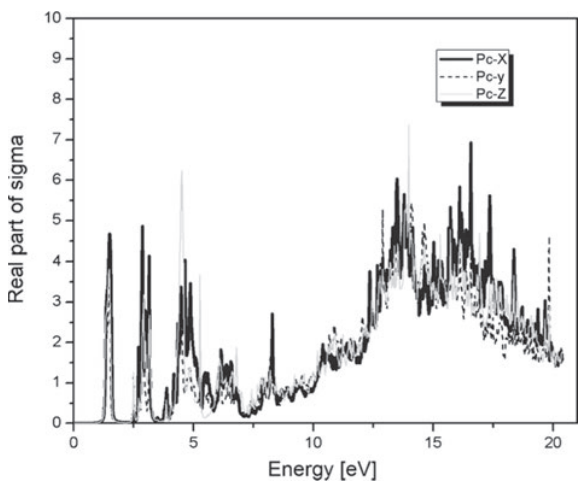


Fig. 9. Optical conduction of metal-free phthalocyanine (H_2Pc).

optical conduction occurs at about 2.48 eV, there is also an optical trap level at 1.48 eV and the refractive index of H_2Pc for all three directions, x-, y- and z-, is illustrated in Figure 10.

We see a small difference in these directions that means, this compound can have birefractive characteristic at these frequencies. In fact, this characteristic has been observed in xy-direction more than in xz-direction. In addition, at high frequencies all directions reach an agreement and there is no birefracting behavior. In order to obtain the static refractive index, we employed the following equation that relates the magnitude of refractive index with dielectric function:

$$n_{\alpha\alpha}(\omega) = \sqrt{\frac{|\varepsilon_{\alpha\alpha}(\omega) + \mathrm{Re}\varepsilon_{\alpha\alpha}(\omega)}{2}}. \quad (4)$$

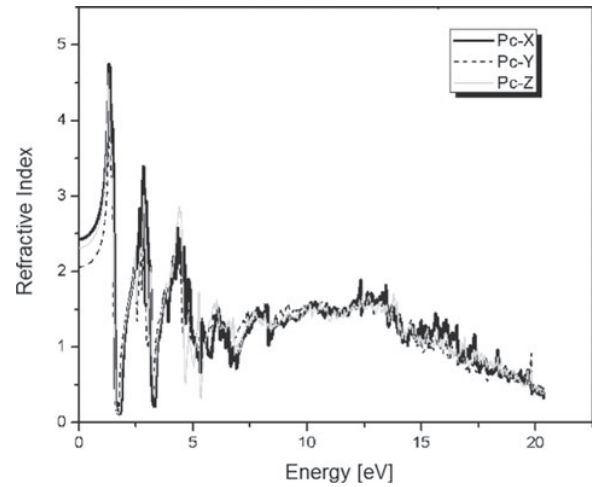


Fig. 10. Refractive index of metal-free phthalocyanine (H_2Pc).

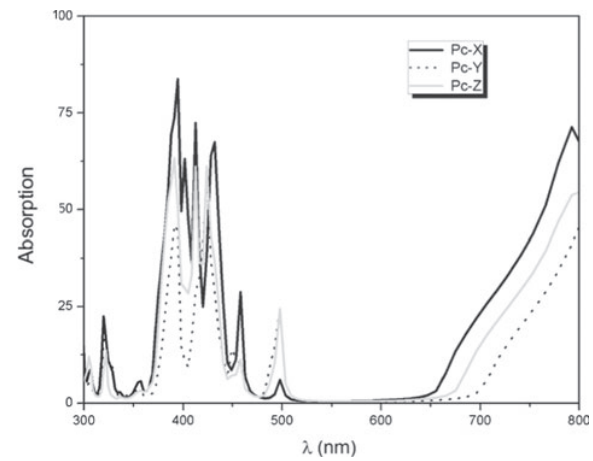


Fig. 11. Absorption index of metal-free phthalocyanine (H_2Pc).

According to this relation and noting that the imaginary part of the dielectric constant vanishes at zero frequency, we obtained the static refractive index in the x-, y- and z-directions as $n_{0xx} = \sqrt{5.91} \approx 2.43$, $n_{0yy} = \sqrt{4.25} \approx 2.06$ and $n_{0zz} = \sqrt{5.36} \approx 2.32$, which are nearly the same as the values of Figure 10 at zero energy. The maximum values of refraction index for x-, y- and z-directions are 4.75, 3.91 and 4.21, respectively, which are gained at the energy of 1.32 eV.

In Figure 11, absorption spectra display the existence of strong absorption bands at the wavelengths of 400 and 800 nm which compare favorably with experiment and it is caused by the $\pi - \pi^*$ transitions of the conjugated macrocycle of 18π electrons [25].

4 Conclusions

A detailed investigation of the band structure and DOS by means of the DFT-GGA method was carried out. Electrical band gap is about 2.4 eV with a trap band.

Samsung Exhibit 1037, Page 5 of 6

The dielectric function, electric loss function, absorption index, optical conductivity and refractive index were calculated. As results: this compound has three plasmon oscillations at energies of 5.21, 3.36 and 1.89 eV and static refractive index in the x-, y- and z-directions is $n_{0xx} = 2.43$, $n_{0yy} = 2.06$ and $n_{0zz} = 2.32$. Absorption spectra display the existence of strong absorption bands in the range of 400 and 800 nm. On the whole, calculated values of band gap and absorption are in good agreement with experiments and the other results for the optical properties await experimental findings for comparison.

References

1. N.M. Amar, R.D. Gould, A.M. Saleh, Curr. App. Phys. **2**, 455 (2002)
2. Z.T. Liu, H.S. Kwok, A.B. Djurišić, J. Phys. D: Appl. Phys. **37**, 678 (2004)
3. B. Brena, C. Puglia, M. de Simone, M. Coreno, K. Tarafder, V. Feyer, R. Banerjee, E. Göthelid, J. Chem. Phys. **134**, 7 (2011)
4. P. Ballirano, R. Caminiti, C. Ercolani, A. Maras, M. Antonietta Orru, J. Am. Chem. Soc. **120**, 12798 (1998)
5. N. Kobayashi, Bull. Chem. Soc. Jpn **75**, 127 (2002)
6. Y. Berredjem, J.C. Bernède, S. Ouro Djobo, L. Cattin, M. Morsli, A. Boulmokh, Eur. Phys. J. Appl. Phys. **44**, 223 (2008)
7. M. Kaneko, T. Taneda, T. Tsukagawa, H. Kajii, Y. Ohmori, Jpn J. Appl. Phys. **42**, 2523 (2003)
8. M. Shah, K.S. Karimovand, M.H. Sayyad, Semicond. Sci. Technol. **25**, 75014 (2010)
9. Y.H. Chen, B.R. Lin, Cambridge J. Online **1270**, 46 (2011)
10. S. Erten, F. Meghdadi, S. Gunes, R. Koeppe, N.S. Sariciftci, S. Icli, Eur. Phys. J. Appl. Phys. **36**, 225 (2006)
11. M.E. Azim-Araghi, M.J. Jafari, S. Barhemat, E. Karimi-Kerdabadi, Sensor Lett. **9**, 1349 (2011)
12. M.E. Azim-Araghi, M.J. Jafari, Eur. Phys. J. Appl. Phys. **52**, 10402 (2010)
13. P.C. Kao, S.Y. Chu, S.J. Liu, Z.X. Youand, C.A. Chuang, J. Electrochem. Soc. **153**, 122 (2006)
14. D. Honholz, S. Steinbrecher, M. Hanack, J. Mol. Struct. **521**, 231 (2000)
15. W. Kohn, L.J. Sham, Phys. Rev. **140A**, 1133 (1965)
16. P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, J. Luitz, WIEN2k, *An Augmented Plane Wave Plus Local Orbital, Program for Calculating Crystal Properties* (Vienna University of Technology, Vienna, Austria, 2008)
17. K. Schwarz, P. Blaha, G.K.H. Madsen, Comput. Phys. Commun. **147**, 71 (2002)
18. J.P. Perdew, S. Burke, M. Ernzerhof, Phys. Rev. Lett. **7**, 195109 (1996)
19. R.L. Kronig, J. Opt. Soc. Am. **12**, 547 (1926)
20. M. Hart, M.S. Thesis, University of Dayton, 2004
21. G.A. Cox, P.C. Knight, J. Phys. Chem. Solids **34**, 1655 (1973)
22. B. Joseph, C.S. Menon, E-J. Chem. **4**, 255 (2007)
23. E. Orti, J.L. Bredas, Synth. Met. **29**, 115 (1989)
24. J. Baedi, M.R. Benam, M. Majidiyan, Phys. Scr. **81**, 5 (2010)
25. B. Joseph, C.S. Menon, E-J. Chem. **5**, 86 (2008)

Samsung Exhibit 1037, Page 6 of 6