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Tuning the Optical, Electronic and Thermal Characteristics of Si_3N_4/PVA/PEO Solid State Structures for Electronics Devices

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The present paper deals with design of Si_3N_4 doped PVA/PEO new structures to use in different optic, electronic, photonic and electric approaches with distinguished characteristics included few costs, high corrosion resistance, lightweight and good optical, thermal and electronic properties. The Si_3N_4/PVA/PEO structures were optimized and effectively simulated with a B3LYP / LanL2DZ primer. The structure stability, optical, thermal and electronic properties of Si_3N_4/PVA/PEO were studied. The obtained results indicated to the PVA/PEO/Si_3N_4 structures may be used for various optoelectronics devices with low cost and high flexibly.

Keywords: silicon nitride, energy gap, PEO, electronic properties, devices.

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Introduction

Ferroelectric materials are characterized by having a polarization direction that can be switched in response to an external electric field, which generates many technical applications [1]. Silicon nitride (Si_3N_4) is an important ceramic material owing to its mechanical, chemical and electronic properties; it has been used in cutting tools, engine components and microelectronic devices due to its excellent mechanical properties [2]. Si_3N_4 is chemically inert and has a wide-band gap with high dielectric constant [3]. The other significant property of Si3N4 is good resistance to oxidation, high hardness, corrosion, high mechanical strength and thermal shock [4]. Gaussian 03 program (computer software which is capable of predicting many properties of molecules and reactions, including the molecular energies and structures) [5] to make the calculation. This work aims to design, structural, optical and electronic characteristics of Si_3N_4 doped PVA/PEO structures for optoelectronics approaches.

I. Theoretical Part

Energy gap refers to energy difference between the (HOMO) and (LUMO) according to the Koopmans theorem [5]:

$$E_{gap} = E_{LUMO} - E_{HOMO}. \quad (1)$$

Ionization potential energy (IP) is defined as[6]:

$$I_E = -E_{HOMO}. \quad (2)$$

Electron affinity can be determined by[5].

$$E_A = -E_{LUMO}. \quad (3)$$

The chemical potential (μ) is calculated by the relation [7]:

$$\mu \approx \frac{1}{2}(E_{HOMO} + E_{LUMO}) \approx -\frac{1}{2}(I_E + E_A). \quad (4)$$

Chemical hardness (H) is calculated by using [8]:

$$H = \frac{I_E - E_A}{2}. \quad (5)$$

Chemical softness (S) is given by the equation [9]:

$$S = \frac{1}{2H}. \quad (6)$$

Electrophilicity (ω) can be defined by [10]:

$$\omega = \frac{\mu^2}{2H}. \quad (7)$$

The electronegativity is given by [11]:

$$E_N = \frac{1}{2}(I_E + E_A). \quad (8)$$

The electric dipole polarizability is the determine of the linear response for the electron density in the existence of electric field [12]. The polarizability is given by [13]

$$< \alpha >= {}^{1}/_{3}\,(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}). \quad (9)$$

II. Results and Discussion

Figure (1) shows find the relaxation of the molecule, in which the optimized structure of the molecule is the structure at minimum energy, and it is performed by finding the first derivative of the energy with respect to distance between different atoms. Table 1 represents the standard orientation of all atoms in the molecule. The bonds values in present work are in a well agreement with [14,15].

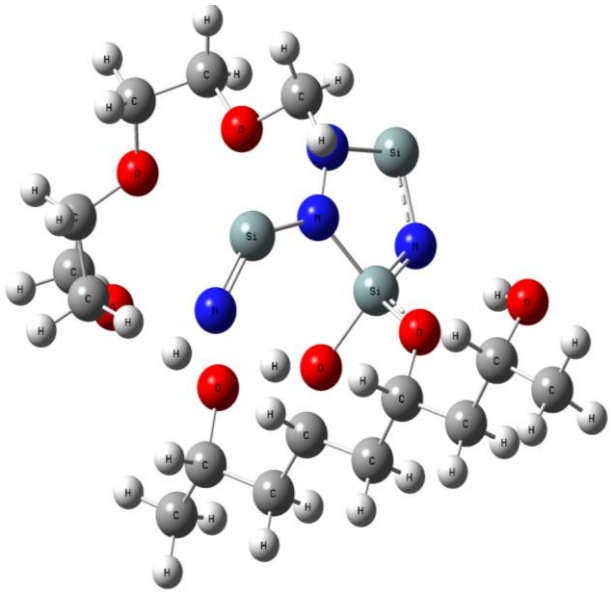

Fig. 1. Optimization of (PVA-PEO-Si_3N_4) structures.

Figure (2) shows the IR-Spectrum of (PVA-PEO-Si_3N_4) structures using DFT. It has been found that the strong peak observed at (2900 cm-1) is attributed to the (O-H) groups. In Raman spectroscopy, a change is observed in the polarization of molecules; that is, a visible or ultraviolet photons interacts with the vibrating molecular bonds, gaining or losing part of their energy, thereby generating the spectrum [15]. Figure (3) shows the Raman spectra of (PVA-PEO-Si_3N_4) structures. Intensities of Raman spectra depend on the probability that photon with particular wavelength will be absorbed.

Table 1.
Average lengths of bond in (Å) and the angles in degree.

Measurements	The optimization parameters	Values
Bonds Å	(C−C)	1.541
	(C−O)	1.480
	(C−H)	1.098
	(O−H)	0.993
	(Si = N)	1.618
	(N−N)	1.401
	(Si−O)	2.730
Angles Deg.	(C−C−C)	112.878
	(C−O−H)	109.132
	(N− Si −N)	101.365

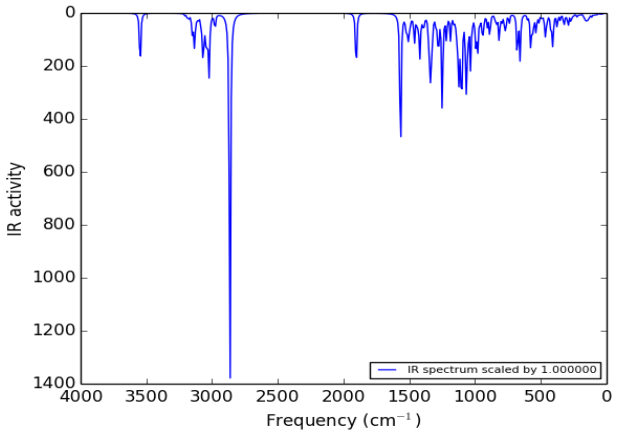

Fig. 2. IR spectra of (PVA-PEO-Si_3N_4) structures.

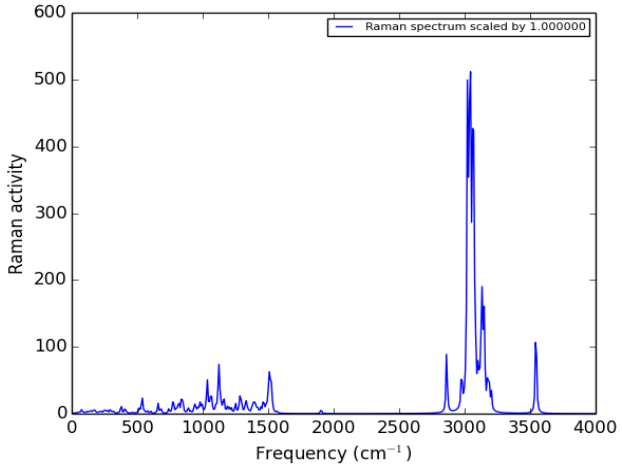

Fig. 3. Raman intensities of (PVA-PEO-Si_3N_4) structures with vibration frequency.

Figure (4) show the UV-Vis spectra Visible and Ultra Violet spectrum is dependent on upon the electronics structure of the molecule. The UV-Vis

calculations of the (PVA-PEO-Si_3N_4) structures obtained from the B3LYP-TD/LanL2DZ method included the excitation energy, wavelength, oscillator strength and electronic transition.

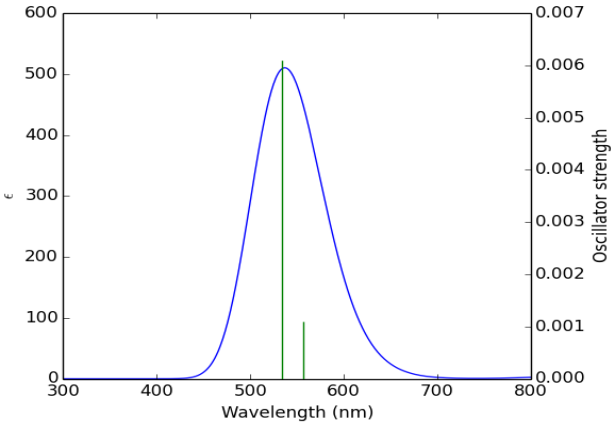

Fig. 4. UV-Vis spectrum for (PVA-PEO-Si_3N_4) structures.

Table. 2 represents the energy gap of (PVA-PEO-Si_3N_4) structures and compared with the experimental data in Ref [17]. Figures (5) illustrates the 3-D distribution of HOMOs and LUMOs for the studied structures. The visualization of HOMO – LUMO obviously characterizes the electron cloud in occupied and virtual orbital. The green color cloud shows the HOMO and red color shows the LUMO electrons in structures. DOS spectrum, the charge density is low in occupied orbital and high in virtual orbital for pure, O and H substituted Si_3N_4 structures. This mentions the localization of charges along the virtual orbitals than in occupied orbitals. The overlapping of Si and N orbitals leads to localization of charges in virtual orbitals. Then the electronic configuration of Si is [Ne] $3s^2$ $3p^2$ and N is $1s^2$ $2s^2$ $2p^3$, when they overlap it gives increase to localization of charges along the virtual orbital.

Table 2.

Energy gap values of in (eV) of structures.

The (PVA-PEO-Si_3N_4) structures		
E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)
-9.341	-2.567	6.773

Figure (6) illustrates the electrostatic surfaces potential (ESP) distribution of structures calculated from the total self-consistent field SCF. ESP distributions of structure are caused by repulsive forces or by attracting regions around each structure. In general, the ESP surfaces of (PVA-PEO-Si_3N_4) structures are dragged toward the negative charge positions in each molecule bases the high electronegativity oxygen atoms [3.5 eV].

Table. 3 shows the results of the ground state energy ET in a. u, the viral ratio (-V/T) is the ratio of the negative magnitude of the potential energy to the kinetic energy and some electronic properties of (PVA-PEO-Si_3N_4) structures calculated at the same level of theory. These properties are included the ionization energy IE, electron affinity EA, electronegativity E_N, electrochemical hardness H and electrophilic index$^{\omega}$ [17].

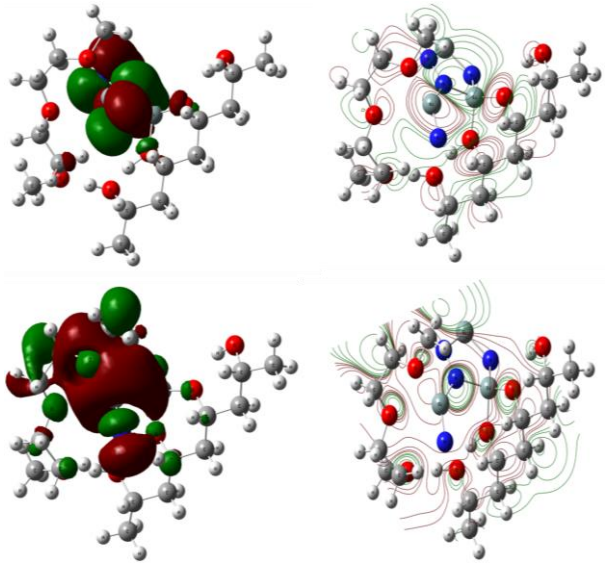

Fig. 5. The distribution of HOMO (up) and LUMO (down) (PVA-PEO-Si_3N_4) structures.

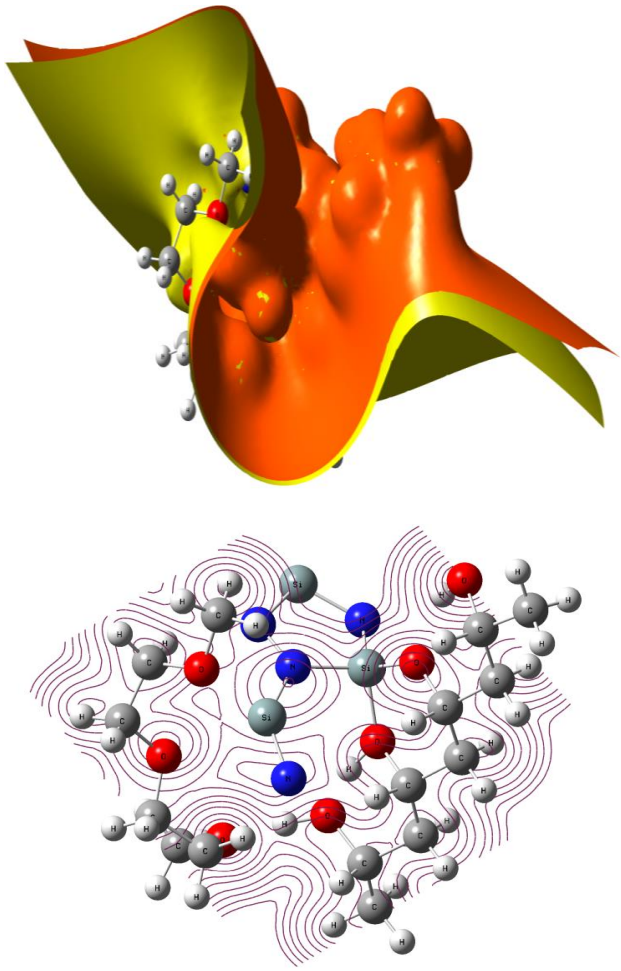

Fig. 6. Electrostatic potential distribution surface for (PVA-PEO-Si_3N_4) structures.

Table.4 shows the average Polarizability αave and it is components in au of (PVA-PEO-Si_3N_4) structures.

Table 3.

Electronic properties values in eV of the structures.

Property	(PVA-PEO-Si_3N_4) composites
Total energy	-1348.406(a.u)
Ionization potential	9.341
Electron affinity	2.567
Electronegativity	5.954
Chemical hardness	3.387
Chemical softness	0.147
Chemical potential	- 5.954
Electrophilicity	5.233
Dipole moment (Debye)	14.168

Table 4.

The calculated α_{ave} and it is components of (PVA-PEO-Si_3N_4) structures.

Polarizability(a.u)			
α_{xx}(a.u)	α_{yy}(a.u)	α_{zz}(a.u)	α_{ave}(a.u)
292.251	294.938	286.380	277.189

The density of states of (PVA-PEO-Si_3N_4) structures as a function of energy levels were calculated by employing the DFT-B3LYP/LanL2DZ level of theory. Figure (7) shows the degenerate states as a function of energy levels for the studied structure, this degeneracy caused by the existence of the new types of atoms, and that leads to varying the bond lengths and angles or changing the geometry of the structure.

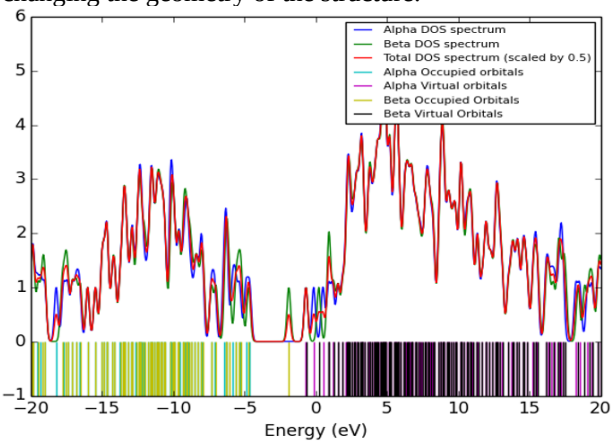

Fig.7. DOS of (PVA-PEO-Si_3N_4) structures.

Table. 5 illustrates the internal thermal energy Eth, specific heat Cv and entropy Sth of (PVA-PEO-Si_3N_4) structures calculated from the same level of theory. These properties are included all the electronic, translational, rotational, vibrational and total thermal properties.

Table 5.

E_{th}, C_v and S_{th} of (PVA-PEO-Si_3N_4) structures.

Thermal corrections (Hartree/Partical)			
	E_{th}(KCal/Mol)	Cv(Cal/Mol-Kelvin)	S_{th}(Cal/Mol-Kelvin)
Electronic	0.000	0.000	1.377
Translational	0.889	2.981	44.300
Rotational	0.889	2.981	36.586
Vibrational	313.331	108.306	132.986
Total	340.065	120.282	134.875

Conclusions

The present work aims to design of Si_3N_4/PVA/PEO new structures to employ in various optoelectronics and photonics approaches with few costs, high corrosion resistance, lightweight and good properties. With the assistance of DFT method, the structures of (PVA-PEO-Si_3N_4) structures are optimized and simulated using B3LYP/LanL2DZ basis set. The structural stability of (PVA-PEO-Si_3N_4) structures are discussed in terms of calculated energy. According to the high of the electrophilicity, the (PVA-PEO-Si_3N_4) structures are more reactive. Finally, the results indicated to the PVA/PEO/Si_3N_4 structures may be used for various optoelectronics devices with low cost, light weight, excellent corrosion resistance and high flexible.

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Х. Ахмед, А Хашім

Налаштування оптичних, електронних та теплових характеристик твердотільних структур Si_3N_4/PVA/PEO для електронних пристроїв

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У роботі розглядаються нові структури PVA/PEO, леговані Si_3N_4, придатні для різних оптичних, електронних, фотонних та електричних застосуваннях із відмінними характеристиками, які включають низьку вартість, високу корозійну стійкість, легку вагу та добрі оптичні, теплові та електронні властивості. Структури Si_3N_4/PVA/PEO оптимізовані та ефективно змодельовані за допомогою праймера B3LYP / LanL2DZ. Досліджено стабільність структури, оптичні, теплові та електронні властивості Si3N4/PVA/PEO. Отримані результати для структур PVA/PEO/Si_3N_4, можуть бути використані для різноманітних оптоелектронних пристроїв із низькою вартістю та високою гнучкістю.

Ключові слова: нітрид кремнію, заборонена зона, PEO, електронні властивості, прилади.