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Clusters of GaAs Prepared by Quantum Mechanical DFT and the Nanowire Raman Spectra

(Penyediaan Kluster GaAs Menggunakan DFT Kuantum Mekanik dan Spektrum Raman Nano Wayar)

AHMAD NAZRUL ROSLI*, HASAN ABU KASSIM & KESHAV N. SHRIVASTAVA

ABSTRACT

We studied the clusters of GaAs by using the density functional theory simulation to optimize the structure. We determined the binding energy, bond lengths, Fermi energy and vibrational frequencies for all of the clusters. We use the Raman data of nanowires of GaAs to compare our calculated values with the experimental values of the vibrational frequencies. The nanowire of GaAs gives a Raman line at 256 cm^{-1} whereas in the bipyramidal Ga_2As_3 the calculated value is 256.33 cm^{-1}. Similarly 285 cm^{-1} found in the experimental Raman data agrees with 286.21 cm^{-1} found in the values calculated for Ga_2As_2 (linear) showing that linear bonds occur in the nanowire. The GaAs is found in two structures zinc-blend as well as wurtzite structures. In the nanowire mixed structures as well as clusters are formed.

Keywords: Cluster; DFT; GaAs; raman spectra; vibrational frequencies

ABSTRAK

Kluster GaAs menggunakan simulasi teori fungsi ketumpatan untuk mengoptimumkan struktur telah dikaji. Tenaga ikatan, panjang ikatan, tenaga Fermi dan frekuensi getaran untuk semua kluster telah diperoleh. Kami menggunakan data Raman untuk nano wayar bagi GaAs untuk membuat perbandingan frekuensi getaran antara hasil pengiraan kami dengan hasil eksperimen. Garis Raman bagi GaAs nano wayar adalah pada 256 cm^{-1} manakala hasil pengiraan kami untuk Ga_2As_3 dwi-piramid adalah 256.33 cm^{-1}. Begitu juga dengan nilai 285 cm^{-1} yang dijumpai pada data eksperimen Raman yang setara dengan hasil pengiraan kami 286.21 cm^{-1} yang dijumpai daripada pengiraan untuk Ga_2As_2 (linear) yang menunjukkan ikatan linear wujud dalam nano wayar. GaAs ditemui dalam dua struktur iaitu zink-blende serta dalam struktur wurtzite. Dalam nano wayar, struktur campuran dan kluster didapati wujud.

Kata kunci: DFT; frekuensi getaran; GaAs; kluster; spektra Raman

INTRODUCTION

The studies of Raman data on GaAs nanowires showed great interest for the past few years (Zardo et al. 2009). Semiconductor nanowires have potential in the electronic devices due to the wide band gap. The metalorganic vapor phase epitaxy (MOVPE) has been used to growth the layer of GaAs nanowire at temperature from 400°C to 500°C (Mohan et al. 2012). The Raman spectroscopy of InAs rich of GaInAsSbP alloy have been reported with TO phonon of GaAs found at 272 cm^{-1} and nearly 290 cm^{-1} for LO phonon (Cheetham et al. 2012). The study of InGaAs and GaAs materials with different pressure until 175 kbar has shown the increasing of phonon shift when they increase the pressure (Whitaker & Dunston 1999). The thin film of GaAs using low-temperature-grown has been discussed and the Raman spectra of GaAs for different temperature has been done (Jiang et al. 1999). It was found that the amorphous phase of arsenic compound from GaAs exists after the annealing.

The density functional theory (DFT) has been widely used to calculate the electronic structure of molecules at the ground state energy (Kohn & Sham 1965). Local density approximation (LDA) and general gradient approximation (GGA) used to treat the interaction of exchange-correlation in the Kohn-Sham equation. We are using DMol3 software provided by Accelerys. This DFT base software has the capability to solve a large system up to 500 atoms. Numerical basis set has been used to predict the minimum energy of molecules. In the past, the calculation of the vibrational frequencies showed a good agreement with the experimental result (Rosli et al. 2009, 2010, 2010, 2011, 2011).

CLUSTER OF GaAs

We prepare the structure by using the density-functional theory. The optimization of the structure leads to the calculation of bond lengths which correspond to minimum energy. The energy is determined by solving the quantum mechanical Schrödinger equation by using the density-functional theory in the local-density approximation (LDA). The stable clusters are shown below.

GaAs (diatomic). This cluster has a bond length of 2.41Å, binding energy of -2.37 eV and the Fermi energy -4.06 eV. It has a stable vibrational frequency (intensity)

TABLE 1. Calculated vibrational frequencies (intensities) of clusters of atoms

No	Cluster	Vibrational frequency (cm^{-1})	Intensity km/mol	Degeneracy
1	$GaAs_2$ (triangular)	64.7	0.24	1
2		188.6	17.78	1
3		345.3	0.19	1
4	Ga_2As (linear)	77.5	0.04	1
5		229.7	4.40	1
6		259.3	1.27	1
7	Ga_2As (triangular)	73.0	0.01	1
8		237.6	4.27	1
9		267.3	1.60	1
10	Ga_2As_2 (linear)	37.6	1.30	2
11		79.2	0.00	2
12		147.7	0.00	1
13		286.2	126.63	1
14		386.2	0.00	1
15	Ga_2As_3 (bipyramidal)	115.5	2.57	2
16		173.5	0.00	2
17		197.7	0.00	1
18		218.6	6.13	1
19		256.3	0.03	1
20		331.9	0.00	1
21	$GaAs_4$ (pyramidal)	62.4	0.95	2
22		75.8	0.00	1
23		144.5	0.31	1
24		271.9	0.00	1
25		274.9	2.30	1
26		277.1	0.70	2

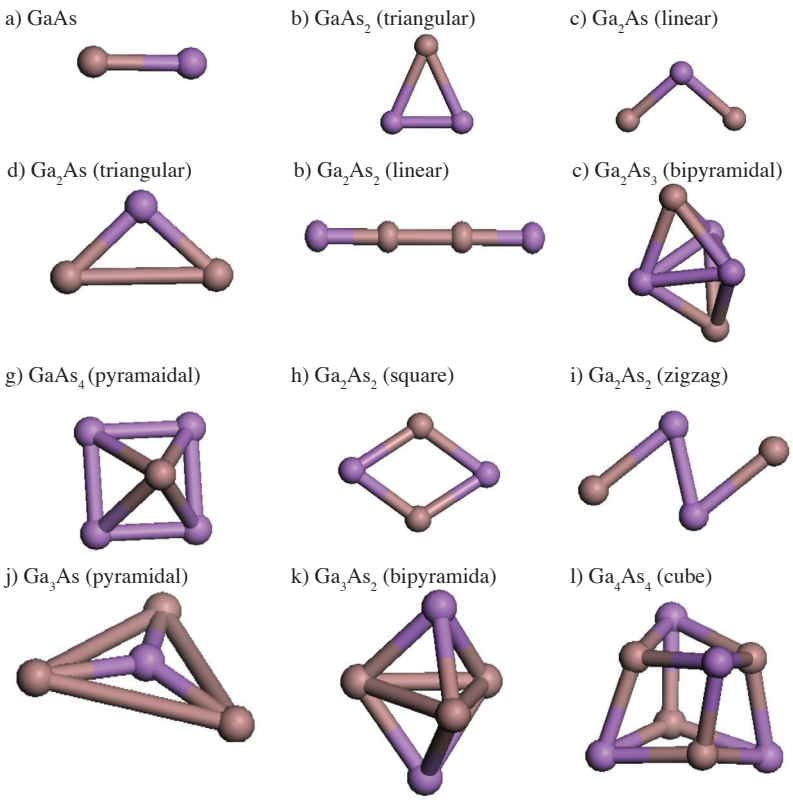

FIGURE 1. The model of several GaAs clusters minimized to optimum geometry

of 208.36 (0.5) cm^{-1} (km/mol) when double numeric wave functions are used. $GaAs_2$ (triangular). In this cluster the bond lengths are GaAs = 2.768Å, As–As = 2.258Å. The binding energy is -6.516 eV and the Fermi energy is -4.079 eV. The vibrational frequencies are given in Table 1. Ga_2As (linear). The linear system has a bond length of 2.397Å, binding energy = -5.68 eV and the Fermi energy of -4.22 eV. The calculated vibrational frequencies are given in Table 1. Ga_2As (triangular). The GaGa bond length is 3.495Å. The binding energy is -5.68 eV and the Fermi energy = -4.2 eV. The calculated vibrational frequencies are given in Table 1. Ga_2As_2 (linear). The bond lengths in this cluster are GaAs = 2.245Å and Ga-Ga distance is 2.354Å. The binding energy is -7.312 eV and the Fermi energy is -4.618 eV. Ga_2As_3 (bipyramidal). This cluster has a bond length 2.610Å for GaAs and As-As distance is 2.661Å. The binding energy is -13.955 eV and the Fermi energy is -4.347 eV. The calculated vibrational spectrum is shown in Figure 1. The vibrational frequencies are given in Table 1. $GaAs_4$ (pyramidal). The bond lengths of this cluster are GaAs = 2.667 Å and AsAs = 2.489 Å. The binding energy is -13.4373 eV and the Fermi energy is -5.141 eV. The vibrational frequencies are given in Table 1.

Ga_2As_2 (square). This cluster has four bonds with the same length. The distance between Ga – As is 2.428 Å. The binding energy is -9.140 eV and the Fermi energy is -4.459 eV. The vibrational frequencies are given in Table 2. Ga_2As_2 (zigzag). This cluster of a linear Ga – As – As – Ga become a zigzag shape when it has been optimized. The bond length for AsAs is 2.388 Å and for the GaAs is 2.665 Å. The binding energy is -3.972 eV while the Fermi energy is -9.93 eV. The calculated vibrational frequencies are given in Table 2. Ga_3As (pyramidal). Three atoms of Ga combined as a triangle shape and bond with As atom at the top. The GaGa bond length is 4.206 Å and the distance for GaAs is 2.438 Å. The binding energy is -8.883 eV and the Fermi energy is -2.886 eV. The calculated vibrational frequencies are given in Table 2. Ga_3As_2 (bipyramidal). The triangle shape of Ga has been built with two As atoms each at the top and bottom of the surface of the triangle. The bond lengths are GaGa = 2.833 Å and GaAs = 2.566 Å. The binding energy is -12.418 eV and Fermi energy is -4.224 eV. The calculated vibrational frequencies are

TABLE 2. Calculated vibrational frequencies (intensities of clusters of atoms)

No	Cluster	Vibrational frequency (cm^{-1})	Intensity km/mol	Degeneracy
1	Ga_2As_2 (square)	47.1	1.40	1
2		140.1	0.05	1
3		158.4	0.26	1
4		247.4	0.00	1
5		279.1	0.03	1
6		313.8	7.12	1
7	Ga_2As_2 (zigzag)	85.2	0.38	1
8		117.2	1.63	1
9		181.9	0.00	1
10		187.3	0.00	1
11		231.8	56.76	1
12		357.7	0.00	1
13	Ga_3As (pyramidal)	28.4	0.78	1
14		54.6	27.84	1
15		55.7	27.94	1
16		219.5	0.06	1
17		325.0	79.58	1
18		325.1	79.69	1
19	Ga_3As_2 (bipyramidal)	86.7	2.11	1
20		87.78	1.88	1
21		129.5	1.73	2
22		212.3	0.00	1
23		217.4	0.01	2
24		327.5	0.00	1
25		333.5	2.13	1
26	Ga_4As_4 (cube)	81.2	0.00	2
27		103.3	11.96	3
28		141.3	0.00	3
29		171.2	1.78	3
30		172.6	0.00	1
31		188.8	0.00	2
32		256.4	0.00	1
33		263.7	22.78	3

TABLE 3. Comparison between calculated values and experimental values

No	Experimental Results (Zardo et al. 2009) (cm^{-1})	Calculated Vibrational Frequencies (cm^{-1})
1	254.0	
2	256.0	256.3 - Ga_2As_3 (bipyramidal)
3	267.2	267.3 - Ga_2As (triangular)
4	285.0	286.2 - Ga_2As_2 (linear)
5	290.0	

given in Table 2. Ga_4As_4 (cube). The bond length for this cluster is 2.539 Å. The binding energy is -24.208 eV and Fermi energy is -4.87 eV. The calculated vibrational frequencies are given in Table 2.

DISCUSSION

The Raman spectra of nanowires give the frequencies as 254 cm^{-1}, 256 cm^{-1}, 266.7 cm^{-1}, 267.2 cm^{-1}, 285 cm^{-1} and 290.9 cm^{-1} as seen from the work of Zardo et al. 2009. The calculated values for Ga_2As_2 (linear) show a stronger line at 286.2 cm^{-1} which agrees with the experimental value of 285 cm^{-1}. This means that linear bonds are present in the nanowire which gives the strength to the wire. The bipyramidal Ga_2As_3 gives the calculated value of 256.3 cm^{-1} to be compared with the experimental value of 256 cm^{-1}. This shows that mixed structures occur in the nanowire. Indeed the GaAs is known to occur in zinc-blend as well as in wurtzite structure. When a nanowire is made new structures occur (Table 3).

We find that clusters are present in a nanowire of GaAs and mixed structures occur. Our previous work (Rosli et al. 2009, 2010, 2010, 2011, 2011) showed that our calculations are reliable.

CONCLUSION

We have performed the *ab initio* calculation of GaAs clusters for the minimum energy. The vibrational frequencies for all clusters of stable atoms have been shown here. The calculation showed a good agreement with the experimental Raman spectra. It showed that the cluster of GaAs exist in the wurtzite material.

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Ahmad Nazrul Rosli*
Faculty Science and Technology
Universiti Sains Islam Malaysia (USIM)
71800 Nilai, Negeri Sembilan
Malaysia

Hasan Abu Kassim & Keshav N. Shrivastava
Department of Physics
University of Malaya
50603 Kuala Lumpur
Malaysia

*Corresponding author; email: anazrul84@yahoo.com

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