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## Article

# Silicon Allotropes, Tetragonal-Body-Centered (bct), Mixed

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**Abstract:** In this work, we will study at a basic level, a series of possible new three-dimensional monoclinic allotropes of silicon, with  $sp^3$  hybridization, of the bct type; where hexahedrons and octahedrons are combined, with other cluster shapes, with basic silicon geometries such as: triangles ( $Si_3$ ), squares ( $Si_4$ ), pentagons ( $Si_5$ ) and hexagons ( $Si_6$ ); similar to two-dimensional,  $sp^2$  hybridized graphene allotropes. Calculating its electron density, bandgap energy and electronic mobility.

**Keywords:** allotropes; materials; semiconductors

## Introduction

Silicon, a basic semiconductor, with a cubic diamond or  $\alpha$  - Si structure, with an indirect bandgap, which is the basis of solid-state electronics, today; because it is abundant, with good physical-chemical properties and is economical; However, it is not the best semiconductor. This has led scientists to look for other allotropic forms of silicon, with high electronic mobility and a direct electronic bandgap, for applications in optoelectronics; to replace silicon, with a diamond structure [1], in electronic applications.

As of 2010, a new form of carbon is described, tetragonal in shape, centered in the body (bct-C<sub>4</sub>) [3] with three-dimensional monoclinic structure and hybridization of chemical bonds,  $sp^3$ ; which is stable at normal pressure. They are made up of flat squares, composed of 4 atoms, which connect with four others, located in the upper corners; and another four, located this time, in the 4 lower corners, of an imaginary tetrahedron, since there is no direct connection, through covalent bond, between the C<sub>4</sub> squares.

There is also a variant of the latter, bct-C<sub>8</sub>, in which, unlike the previous one, the atoms form octagonal rings in this phase. These phases are semiconductors, with an indirect bandgap of 1.66 eV.

In this work, we will study basic aspects of electronic density, effective mass, energy gap and electronic mobility, which characterize the silicon bct allotropes, similar to the different graphene allotropes; where different plane figures are combined, forming a two-dimensional mosaic of  $sp^2$  hybridization, in this case.

## 2. Calculation Model

The electrons that move freely through the solid, from the electrons of density, were established by the free electron gas model of Drude and Sommerfeld [4,5].

$$n_e = N_A \sum_A \frac{Z}{A} \rho_m \quad (1)$$

$N_A$ , is Avogadro's number or constant,  $Z$  indicates the electronic valence number,  $A$  is the atomic mass of the chemical element (in g/mol),  $\rho_m$ , is the mass density (mass, divided by volume) and  $n_e$ , They are the conduction electrons, or number of free electrons. This is the basic equation to calculate its concentration.

For a unit cell, we can simplify the equation to the form:

$$\frac{n_e}{N_A} = \left( \frac{Z}{A} \right) n^0_A \quad (2)$$

In this equation, we replace the mass density,  $\rho_m$ , with  $n^0_A$ , which is the number of atoms that make up the unit cell [6].

The effective or dynamic mass of the electron is defined by the formula:

$$m^* = \frac{\sigma}{e^2 \tau} = \sqrt{n_e} \quad (3)$$

where,  $m^*$ , is the effective mass of the electrons,  $\sigma$ , is the electronic conductivity,  $e$ , is the charge of an electron, and  $\tau$ , is the Relaxation Time; which is the average time between consecutive collisions of an electron. It is an average value, since not all collisions occur at regular intervals.

There is a relationship between this effective or dynamic mass of free electrons in motion, and the forbidden energy gap or band gap [7].

$$m^* \sim E_g \quad (4)$$

And between these and electronic mobility [7], which measures the efficiency of semiconductors.

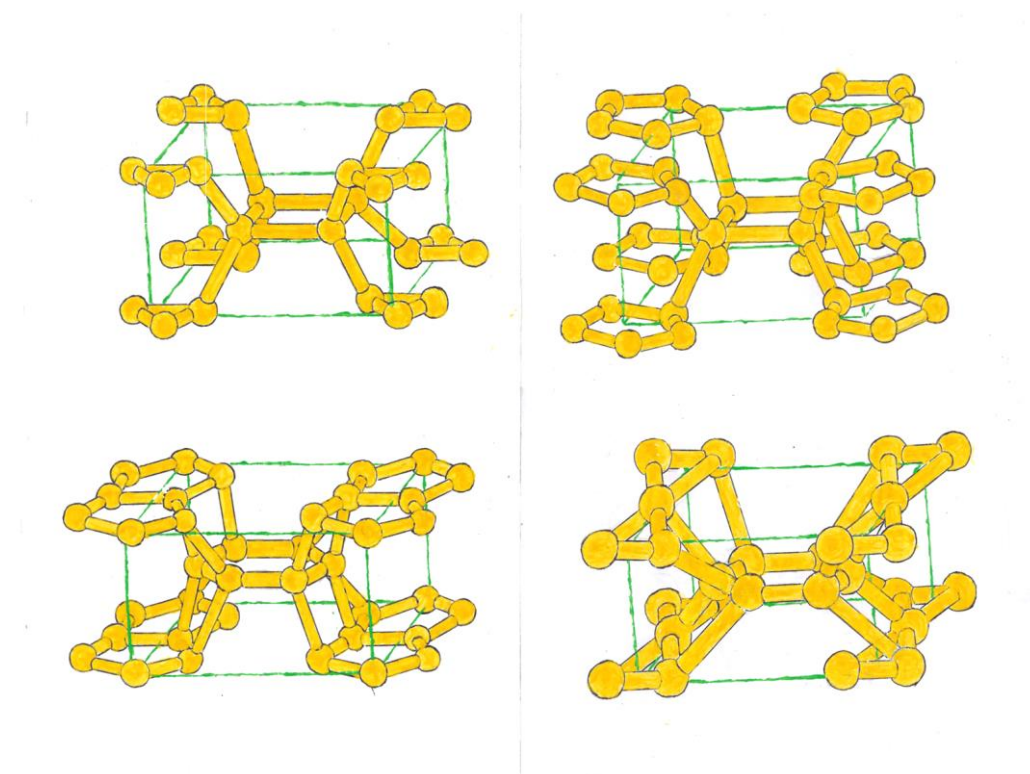
$$\mu \sim \frac{1}{m^*} \sim \frac{1}{E_g} \quad (5)$$

From these basic equations, we can calculate many materials.

### 3. Structure

In this case, we have bcts, formed by central rings of 4 silicon atoms, combined with other rings, formed by 3, 5, or 6 atoms. (Figure 1, top).

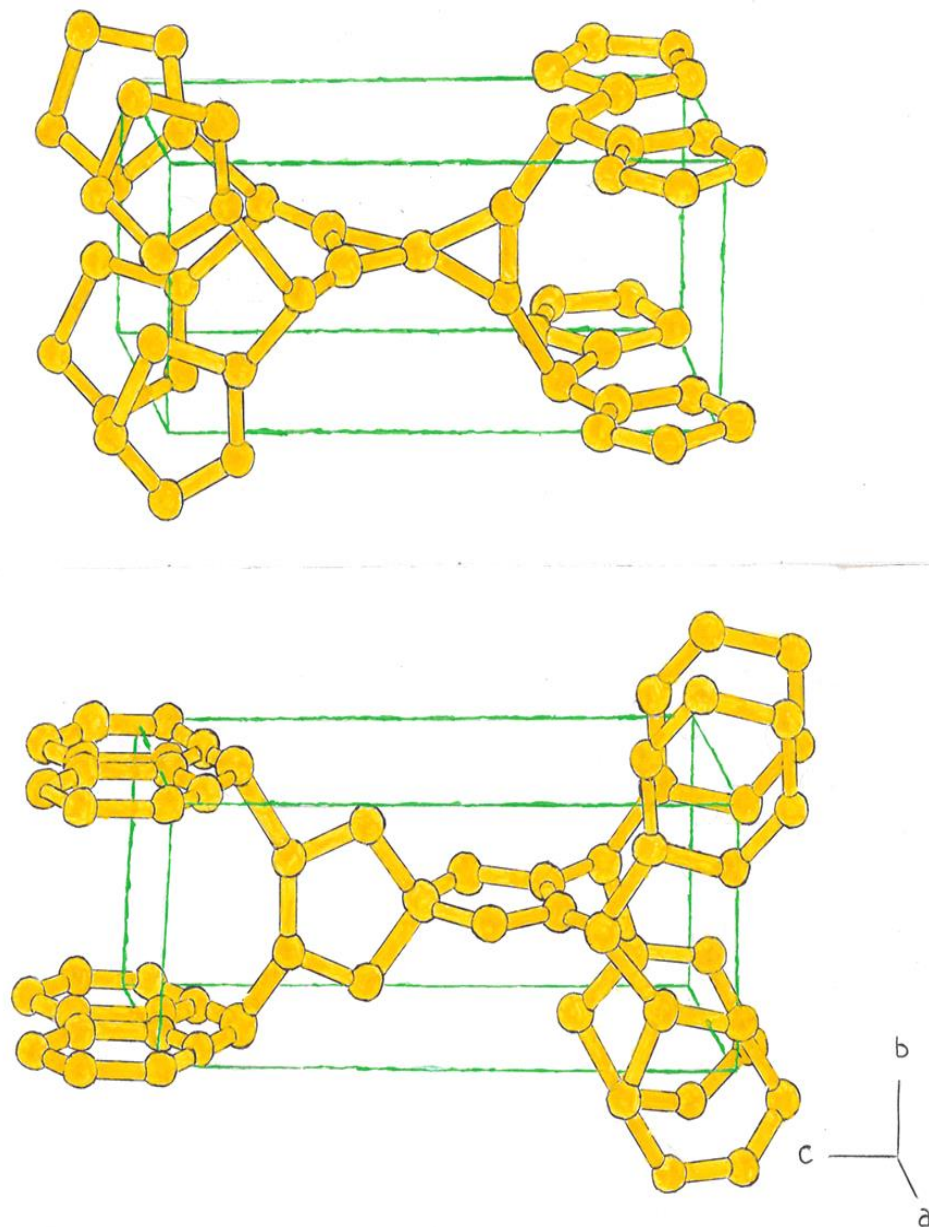
In the second case, we have bcts, in which the central ring is formed by rings of 6 atoms, combined with rings that can be composed of 3, 4 and 5 atoms, at the ends of the imaginary tetrahedron (Figure 1, in the bottom.)



**Figure 1.** Mixed Silicon Bcts. Bct Si<sub>4</sub>: Si<sub>4</sub> - Si<sub>3</sub>, ( Si<sub>7</sub> ) and Si<sub>4</sub> - Si<sub>5</sub>, ( Si<sub>9</sub>), at the top; and bct Si<sub>6</sub>: Si<sub>6</sub> - Si<sub>5</sub>, ( Si<sub>11</sub> ) and Si<sub>6</sub> - Si<sub>3</sub>, ( Si<sub>9</sub> ), at the bottom.

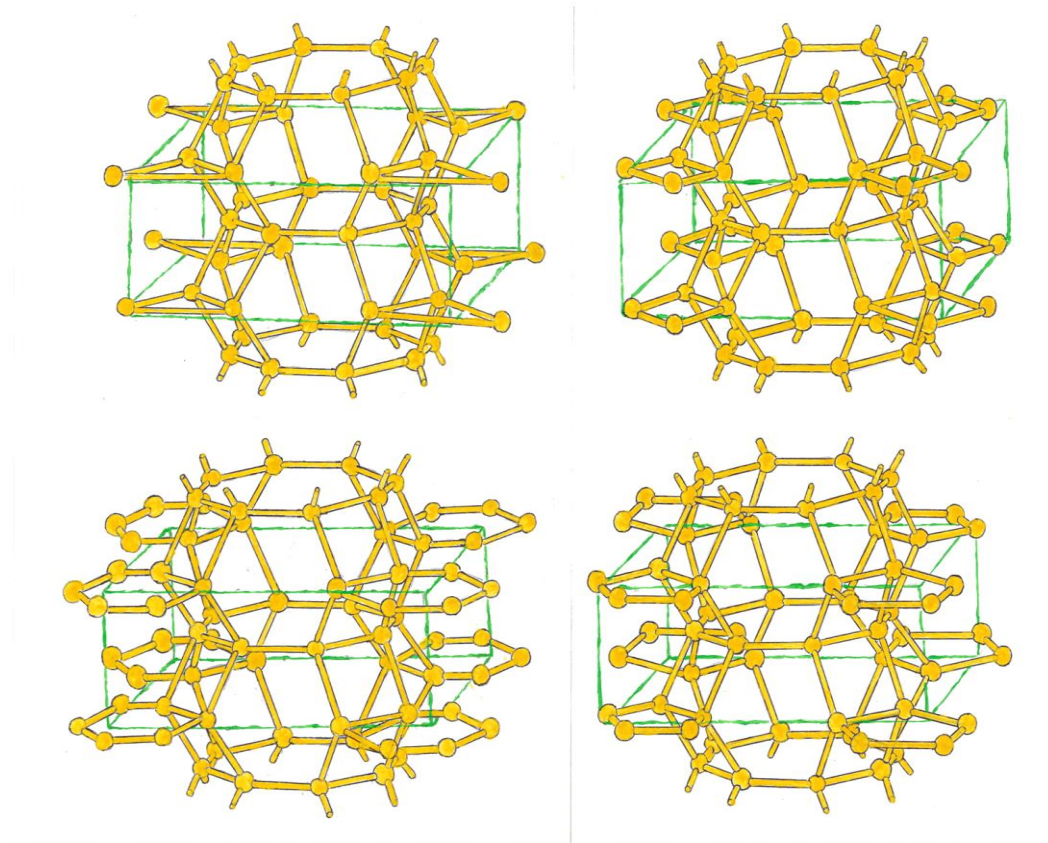
We can also form bcts, where two converging triangles link with 4 atoms, centered on the faces of an imaginary tetragon. These atoms, in turn, link with 4 rings that can be composed of 4, 5 and 6 silicon. (Figure 2, top.)

In the second group, two convergent pentagonal rings, as in the previous one, link with 4 atoms that center the faces of an imaginary tetrahedron. These atoms, in turn, can link with rings formed by 3, 4, 6, 7 and 8 atoms, which will be located at the ends of the tetrahedron. (Figure 2, at the bottom.)



**Figure 2.** Mixed Bcts. Bct Si<sub>5</sub>: Si<sub>5</sub> - Si<sub>2</sub> - Si<sub>5</sub> ( Si<sub>12</sub>), ( pentagons ), at the top; and bct Si<sub>8</sub> - Si<sub>2</sub> - Si<sub>6</sub>, ( Si<sub>16</sub>), at the bottom.

Finally, a third group of bcts, formed by Si<sub>8</sub> octahedra, can bond with rings of 3, 4, 5, 6 and 7 atoms, in an imaginary tetrahedron (Figure 3).



**Figure 3.** Mixed Bct<sub>s</sub>, Si<sub>8</sub>: Si<sub>8</sub> - Si<sub>3</sub>, ( Si<sub>11</sub> ); Si<sub>8</sub> - Si<sub>4</sub>, ( Si<sub>12</sub> ); Si<sub>8</sub> - Si<sub>5</sub>, ( Si<sub>13</sub> ) and Si<sub>8</sub> - Si<sub>6</sub>, ( Si<sub>14</sub> ).

#### 4. Results of Electrical Characteristics

In this work, basic calculations will be carried out for the results tables, in density of free electrons, their effective mass, as well as their mobility; that will be presented below.

**Table 1.** Results of calculation of the basic electronic parameters of mixed bcts.

| Allotrope                                           | $n^{\circ}_A$ | Z | A        | $\frac{n_e}{N_A}$ | $m^*$   | $E_g$<br>( Ev ) | $\mu$<br>( $\frac{1}{Vs}$ ) |
|-----------------------------------------------------|---------------|---|----------|-------------------|---------|-----------------|-----------------------------|
| <hr/>                                               |               |   |          |                   |         |                 |                             |
| ( triangular )                                      |               | 4 | 28. 0855 |                   |         |                 |                             |
| Si <sub>5</sub> - Si <sub>2</sub> - Si <sub>4</sub> | 11            |   |          | 1. 5664           | 1. 2515 | 1. 2515         | 0. 7990                     |
| Si <sub>5</sub> - Si <sub>2</sub> - Si <sub>5</sub> | 12            |   |          | 1. 7088           | 1. 3072 | 1. 3072         | 0. 7649                     |
| Si <sub>5</sub> - Si <sub>2</sub> - Si <sub>6</sub> | 13            |   |          | 1. 8512           | 1. 3605 | 1. 3605         | 0. 7350                     |
| <br>( squares )                                     |               |   |          |                   |         |                 |                             |
| Si <sub>4</sub> - Si <sub>3</sub>                   | 7             |   |          | 0. 9968           | 0. 9983 | 0. 9983         | 1. 001                      |
| Si <sub>4</sub> - Si <sub>5</sub>                   | 9             |   |          | 1. 2816           | 1. 1320 | 1. 1320         | 0. 8833                     |
| Si <sub>4</sub> - Si <sub>6</sub>                   | 11            |   |          | 1. 5664           | 1. 2515 | 1. 2515         | 0. 7990                     |
| <br>( pentagonal )                                  |               |   |          |                   |         |                 |                             |
| Si <sub>9</sub> - Si <sub>2</sub> - Si <sub>3</sub> | 14            |   |          | 1. 9936           | 1. 4119 | 1. 4119         | 0. 7082                     |
| Si <sub>9</sub> - Si <sub>2</sub> - Si <sub>4</sub> | 15            |   |          | 2. 136            | 1. 4614 | 1. 4615         | 0. 6842                     |

**Table 1.** ( continue ).

| <hr/>      |               |   |          |                   |       |        |       |
|------------|---------------|---|----------|-------------------|-------|--------|-------|
| Allotrope  | $n^{\circ}_A$ | Z | A        | $\frac{n_e}{N_A}$ | $m^*$ | $E_g$  | $\mu$ |
| ( x cell ) |               |   |          |                   |       | ( Ev ) |       |
| <hr/>      |               |   |          |                   |       |        |       |
|            |               | 4 | 28. 0855 |                   |       |        |       |

|                                                     |    |         |         |         |         |
|-----------------------------------------------------|----|---------|---------|---------|---------|
| Si <sub>9</sub> - Si <sub>5</sub> - Si <sub>2</sub> | 16 | 2. 2784 | 1. 5094 | 1. 5094 | 0. 6625 |
| Si <sub>9</sub> - Si <sub>2</sub> - Si <sub>6</sub> | 17 | 2. 4208 | 1. 5558 | 1. 5558 | 0. 6427 |

( hexagonal )

|                                   |    |         |         |         |         |
|-----------------------------------|----|---------|---------|---------|---------|
| Si <sub>6</sub> - Si <sub>3</sub> | 9  | 1. 2816 | 1. 1320 | 1. 1320 | 0. 8833 |
| Si <sub>6</sub> - Si <sub>4</sub> | 10 | 1. 424  | 1. 1933 | 1. 1933 | 0. 8380 |
| Si <sub>6</sub> - Si <sub>5</sub> | 11 | 1. 5664 | 1. 2515 | 1. 2515 | 7990    |

( octogonal )

|                                   |    |         |         |         |         |
|-----------------------------------|----|---------|---------|---------|---------|
| Si <sub>8</sub> - Si <sub>3</sub> | 11 | 1. 5664 | 1. 2515 | 1. 2515 | 0. 7990 |
| Si <sub>8</sub> - Si <sub>4</sub> | 12 | 1. 7088 | 1. 3072 | 1. 3072 | 0. 7649 |
| Si <sub>8</sub> - Si <sub>5</sub> | 13 | 1. 8512 | 1. 3605 | 1. 3605 | 0. 7350 |
| Si <sub>8</sub> - Si <sub>6</sub> | 14 | 1. 9936 | 1. 4119 | 1. 4119 | 0. 7082 |

Table 1. Result of calculations of the basic electronic parameters of mixed bcts.

Conclusions

The mixed, tetragonal, body-centered allotropes (bct), which have an energy gap closer to that of the diamond form of silicon (calc.: 1.0673, exp.: 1.1 eV), are: Si<sub>4</sub> - Si<sub>5</sub>, square (1, 1320 eV), and Si<sub>6</sub> - hexagonal Si<sub>3</sub> (1, 1320 eV). The others have an energy gap, somewhat below that reached by the atoms that form a diamond-type crystal, in the case of Si<sub>4</sub> - Si<sub>3</sub>; with an E<sub>g</sub> of 0.9983 eV; the triangular Si<sub>6</sub> - Si<sub>3</sub>, the hexagonal Si<sub>6</sub> - Si<sub>5</sub> and the octagonal Si<sub>8</sub> - Si<sub>3</sub> (1, 2515 eV), are a little away from the energy gap of diamond. Others such as the hexagonal Si<sub>6</sub> - Si<sub>4</sub> (1, 1933 eV); Si<sub>5</sub> - Si<sub>5</sub>-Si<sub>2</sub>, triangular (1, 3072 eV), Si<sub>8</sub> - Si<sub>6</sub>, octagonal (1, 4119 eV), or Si<sub>9</sub> - Si<sub>5</sub> - Si<sub>2</sub>, pentagonal (1, 5094 eV), are already further from the gap energy E<sub>g</sub>, of the diamond. Other allotropes such as the hexagonal or lonsdaleite form of silicon, Si-4H, have an energy gap (E<sub>g</sub>) of 1.2 eV.

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