Materials Research Express

PAPER

Synthesis of new Si_9 material with a direct bandgap and its unique physical properties

To cite this article: Wei-Qi Huang *et al* 2019 *Mater. Res. Express* **6** 105905

Materials Research Express

PAPER

Synthesis of new Si_9 material with a direct bandgap and its unique physical properties

RECEIVED
13 June 2019

REVISED
23 July 2019

ACCEPTED FOR PUBLICATION
6 August 2019

PUBLISHED
21 August 2019

Wei-Qi Huang[1], **Zhong-Mei Huang**[2], **Shi-Rong Liu**[3] **and Hong-Yan Peng**[1]

[1] Department of Physics, Hainan Normal University, Haikou 571158, People's Republic of China
[2] College of materials and metallurgy, Institute of Nanophotonic Physics, Guizhou University, Guiyang 550025, People's Republic of China
[3] State Key Laboratory of Environment Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550003, People's Republic of China

E-mail: wqhuang@gzu.edu.cn

Keywords: new allotrope, coherent electron beam, pulsed laser deposition

Abstract

Even though economic advantages of silicon still keep it as the dominant material for the solar cell industry in the near future, crystal silicon in the diamond structure (d-Si) is an indirect bandgap semiconductor which prevents to consider it as a next-generation platform for optical material technologies. Here, we report the formation of a new allotrope of silicon on surface, Si_9, using a novel two-step synthesis methodology. First, a film of amorphous silicon was produced by using pulsed laser deposition method, and second, new Si_9 was synthesized under irradiation of coherent electron beam on the amorphous Si film. It is important that the structure of Si_9, forming six-membered sp3 silicon rings and involving 9 silicon atoms in one unit, possesses a direct bandgap near 1.59 eV, around which we have measured the emission peak in photoluminescence spectra on the pure Si_9. It is discovered that Si_9 can be easily doped as both p- and n-type on surface, where boron and nitrogen are demonstrated as the most promising elements for the p-type and n-type doping in Si_9, respectively, due to their low formation energies and reductions in the band gap. These properties suggest great potential in constructing a novel Si_9-based p-n junction which is highly desired for future industrial application of optoelectronic technologies and photovoltaic devices.

1. Introduction

We all know that silicon is a main stay of semiconductor technology because of the elemental abundance, lower costs, and ability for doping of p and n type. The indirect gap (1.12 eV) of Si with diamond structure (d-Si) needs phonons to mediate electronic excitations from visible and infrared light, which prevents silicon from being considered as a next-generation platform for applications such as thin-film photovoltaic devices [1] and light-emitting diodes [2–5]. A lot of investigations have been motivated by the potential to find new silicon allotropes with advanced optoelectronic properties beyond those of d-Si [1, 6, 7]. For example, photovoltaic applications ideally require a direct bandgap of ~1.2 ~ 2.5 eV [8, 9], which have not been achieved by any existing silicon phase. Recently, low-energy silicon allotrope candidates were suggested that exhibit greatly improved visible light absorption characteristics with quasi direct bandgaps and direct gaps, however, no experimental synthesis of new silicon allotropes with direct gaps has been reported thus far [1, 10, 11]. It was reported that the formation of Na_4Si_{24} provides a possible path way to produce a new Si_{24} structure with quasi direct bandgaps [12–16]. And further studies were continued to evaluate Si_{24} for solar energy application, such as forming a p−n junction for solar cell application [17–21].

In the article, we report the discovery of a new allotrope of silicon on surface, Si_9, formed through a novel two-step synthesis methodology, which involves a film of amorphous silicon produced by using pulsed laser deposition (PLD) method, and the new Si_9 synthesized under irradiation of coherent electron beam on the amorphous Si film. We have discovered that the structure of Si_9, forming six-membered sp3 silicon rings and involving 9 silicon atoms in one unit, possesses a direct bandgap near 1.59 eV, which is well within the optical

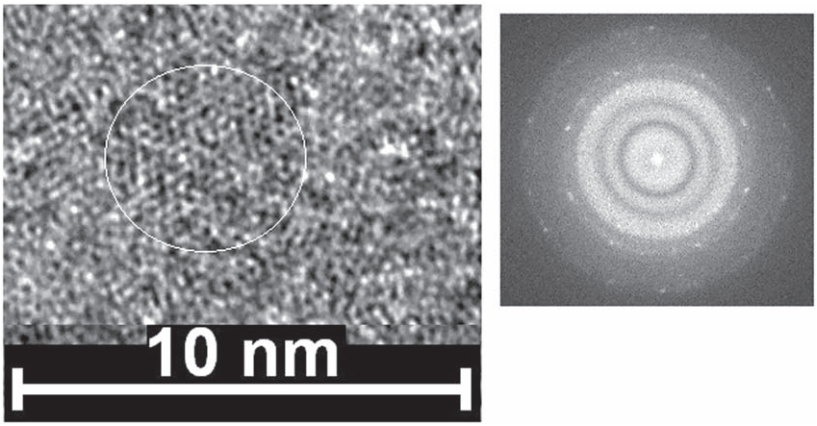

Figure 1. (a) TEM image of the new Si_9 structure, in which the six-membered sp3 silicon rings occur in the white circle. (b) The electronic diffraction pattern of the Si_9 structure.

bandgaps for photovoltaic applications. It is important that Si_9 can be easily doped as both p- and n-type on surface, in which it has been demonstrated for boron and nitrogen to be as the most promising elements of the p-type and n-type doping in Si_9, respectively. The low formation energies and the reductions of the band gap (near 0.78 $\sim$ 0.89 eV) can be obtained in the Si_9 doped with boron and nitrogen, which has a good application in optical communication window.

2. Experiment

In our experimental observation, the TEM image of figure 1(a) shows the new Si_9 structure where there are six-membered sp3 silicon rings observed in the white circle. And the electronic diffraction pattern of the Si_9 structure is exhibited in figure 1(b). In the synthesizing process of the new Si_9, at first, a film of amorphous silicon was produced on P-type (100) oriented substrate with 10 Ω cm by using PLD method with a third harmonic of pulsed Nd:YAG laser at 355 nm, and then a new allotrope of silicon, Si_9, was synthesized under irradiation of coherent electron beam on the amorphous Si film for suitable time in the Tecnai G2 F20 system, in which electron beam from field-emission electron gun, was accelerated by 200 KV.

In the synthesizing process, a silicon wafer was taken on the sample stage in the combination fabrication system with PLD devices. On the surface, a third harmonic of pulsed Nd:YAG laser at 355 nm was used to deposit the amorphous silicon film in PLD process. The amorphous silicon film was exposed under the coherent electron beam with 0.5 nA nm^{-2} for suitable time in the Tecnai G2 F20 system, in which the coherent electron beam from field-emission electron gun has higher energy and better coherent. After irradiation under the coherent electron beam for 25 min, the new Si_9 structure gradually grows on the amorphous silicon film, where the six-membered sp3 silicon rings and the nine Si atoms unit are built.

We have built the boron and nitrogen gas tubes into the chamber of the PLD device for doping as both p- and n-type on Si_9 surface respectively, which can affect their electronic structures. It is interesting to make a comparison between the pure Si_9 structure and the Si_9 doped with nitrogen or boron. In the photoluminescence (PL) spectra, it should be noted that the region of emission wavelength is from 600 nm to 900 nm on the pure Si_9 structure, and the emission peak occurs near 1850 nm in PL spectra at room temperature on the Si_9 structure doped with nitrogen. The PL spectra on the samples were measured under Ar ion laser at 514 nm or 488 nm excitation at room temperature (300 K) and lower temperature (17 K) in sample chamber of 1 Pa. The visible spectrum on the pure Si_9 structure and the infrared spectrum on the Si_9 structure doped with nitrogen were respectively measured for identifying the related electronic states.

3. Simulating calculation

We have built a model in order to simulate the structure of the new Si_9 according to its TEM image, as shown in figure 2(a), where there are nine silicon atoms in an unit (white circle), the bond angle is about 110° and the bond length is about 0.24 nm in the six-membered sp3 silicon rings. Figure 2(b) exhibits the atomic diagram of the new Si_9 structure. The electronic behavior is investigated by an *ab initio* non relativistic quantum mechanical analysis in this work. The density of functional theory (DFT) calculation was carried out by using the local density approximation (LDA) and gradient-corrected exchange-correlation function (GGA) for the

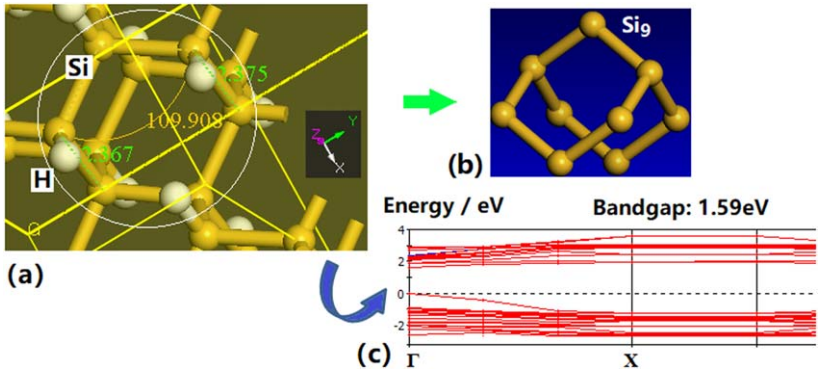

Figure 2. (a) A structure model of the new Si_9 according to its TEM image, where there are nine silicon atoms in an unit (white circle), the bond angle is about 110° and the bond length is about 0.24 nm in the six-membered sp3 silicon rings, in which the yellow ball describes silicon atom and the white ball relates to hydrogen atom for passivation. (b) Atomic diagram of the new Si_9 structure. (c) A energy band structure with direct gap obtained for a good passivation of Si-H bonds on the Si_9 surface in the result of the simulating calculation, where the direct gap is about 1.59 eV.

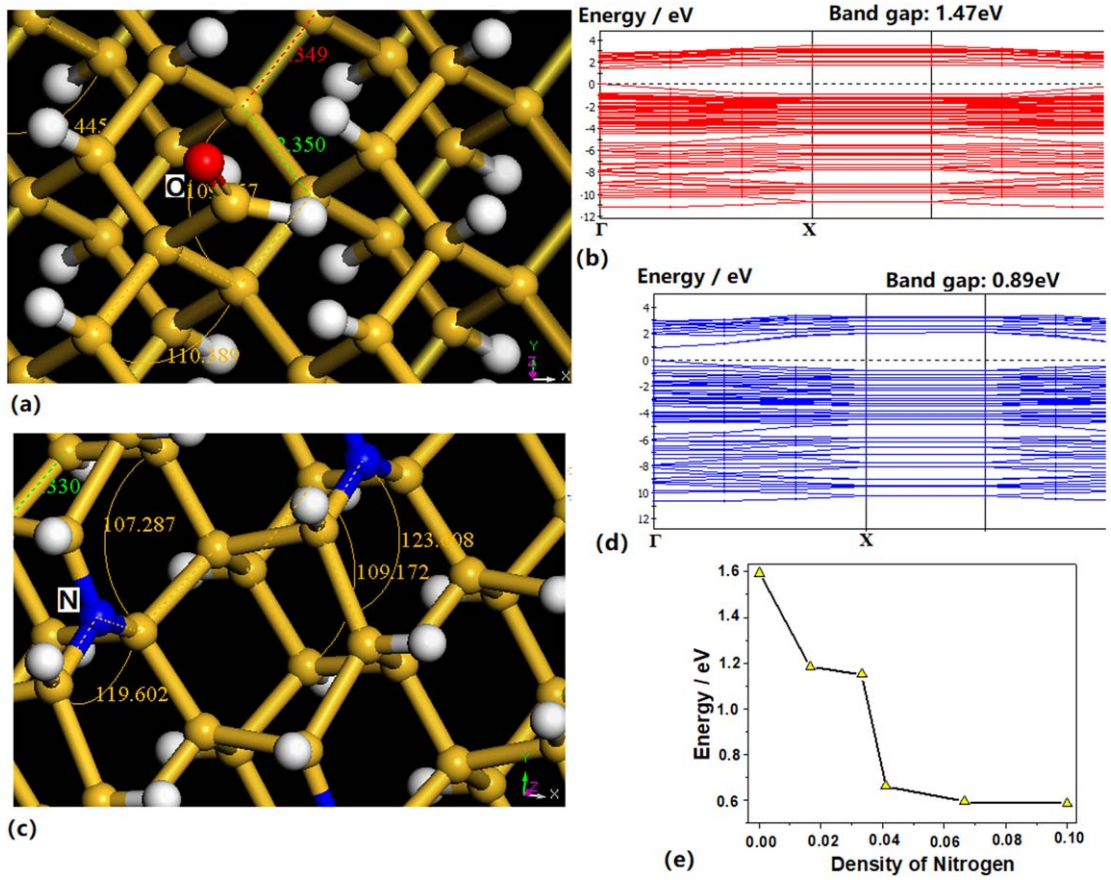

Figure 3. (a) A structure model of the Si_9 doped with oxygen atom (red ball) on surface, where a little change occurs in angle and length of bonds after optimum process (b) the direct bandgap structure with narrower gap of 1.47 eV obtained in the simulating calculation. (c) A structure model of the Si_9 doped with nitrogen (blue ball) built on surface, where the larger angle of Si—N—Si bond is about 123° occurring after the optimum process. (d) Its direct bandgap structure with the narrower gap of 0.89 eV in the calculation result, which will have a good application in optical communication. (e) The change curve of bandgap width with increasing density of doping nitrogen, in which the nonlinear quantum change was obviously observed in the evolution of band gap width in the Si_9 doped with nitrogen on surface.

self-consistent total energy calculation. In the simulating calculation, a energy band structure with direct gap is obtained for a good passivation of Si-H bonds on the Si_9 structure, as shown in figure 2(c), where the direct gap is about 1.59 eV which should have a good application in the optical bandgaps for photovoltaic material.

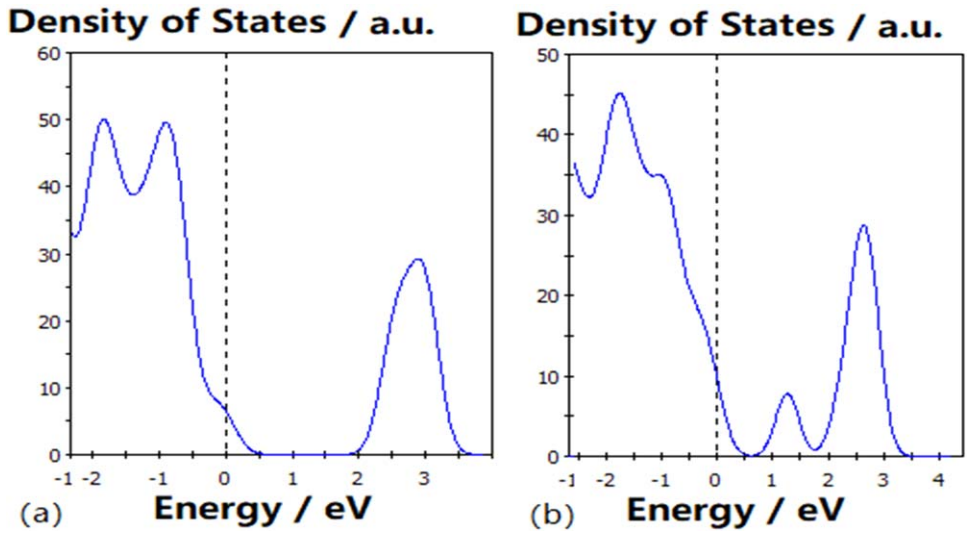

Figure 4. The density distribution pictures of the electronic states in the structure models of the pure Si_9 (a), and the Si_9 doped with nitrogen (b) in which the localized states obviously occur in band gap.

First-principles total-energy calculations were used to optimize the equilibrium geometries and the relative energies of the simulation models in the Si_9 structure. The simulating calculation was performed in the structure model of the six-membered sp3 silicon rings, and vacuum region of at least 1 nm. All atomic positions were relaxed, except the bottom Si layer and its passivating hydrogen layer.

The new Si_9 material can be easily doped n-type elements such as oxygen or nitrogen, which can affect its electronic structure. As shown in figure 3(a), we have built the Si_9 doped with oxygen atom (red ball), in which a little change occurs in angle and length of bonds after optimum process. In the simulating calculation, the direct bandgap structure with narrower gap of 1.47 eV is obtained, as exhibited in figure 3(b).

Our calculations predict that n-type Si_9 can be easily achieved by doping with group V elements, particularly nitrogen. A structure model of Si_9 doped with nitrogen (blue ball) has been built, where the larger angle of Si–N–Si bond is about 123° on surface after the optimum process, as shown in figure 3(c). And the calculation result exhibits that the direct bandgap structure with the narrower gap of 0.89 eV can be obtained, as shown in figure 3(d), which will have a good application in optical communication.

It should be noted that the width change on bandgap was obviously observed with increasing nitrogen density on surface of the Si_9, as shown in figure 3(e), where it is interesting that the nonlinear quantum change occurs in the evolution of bandgap width with various doping density of nitrogen. It may be originated from some quantum effect.

It is interesting to make a comparison of density distributions of the electronic states between the pure Si_9 structure and the Si_9 doped with nitrogen in the simulating calculation. We have noted the obvious change of the density of electronic states, where figure 4(a) shows the density distribution of the electronic states in the pure Si_9 structure, and figure 4(b) exhibits the density distribution of the electronic states in the Si_9 doped with nitrogen on surface in which the localized states obviously occur in band gap.

The calculation result dedicates that p-type Si_9 can be easily achieved by doping with group III elements, particularly boron. The structure model of the Si_9 doped with boron on surface is shown in figure 5(a), in which the larger angle of Si–B–Si bond is about 122° on surface after the optimum process. Its density of states is exhibited in figure 5(b), where the localized states occur near the valence band. And its energy band with narrower direct bandgap is shown in figure 5(c) where the bandgap deceases to 0.78 eV. On the basis of these properties, we will expect that the p−n junction of Si_9 can be easily fabricated for a good solar cell material and optoelectronic devices.

4. Measurement

According to the results of the simulating calculation, the direct bandgap of the pure Si_9 occurs near 1.5 eV, around which we have measured the emission peak in PL spectra on the sample of the pure Si_9 at room temperature, as shown in figure 6, in which the light beam at 514 nm in Ar ion laser is used for excitation. Here,

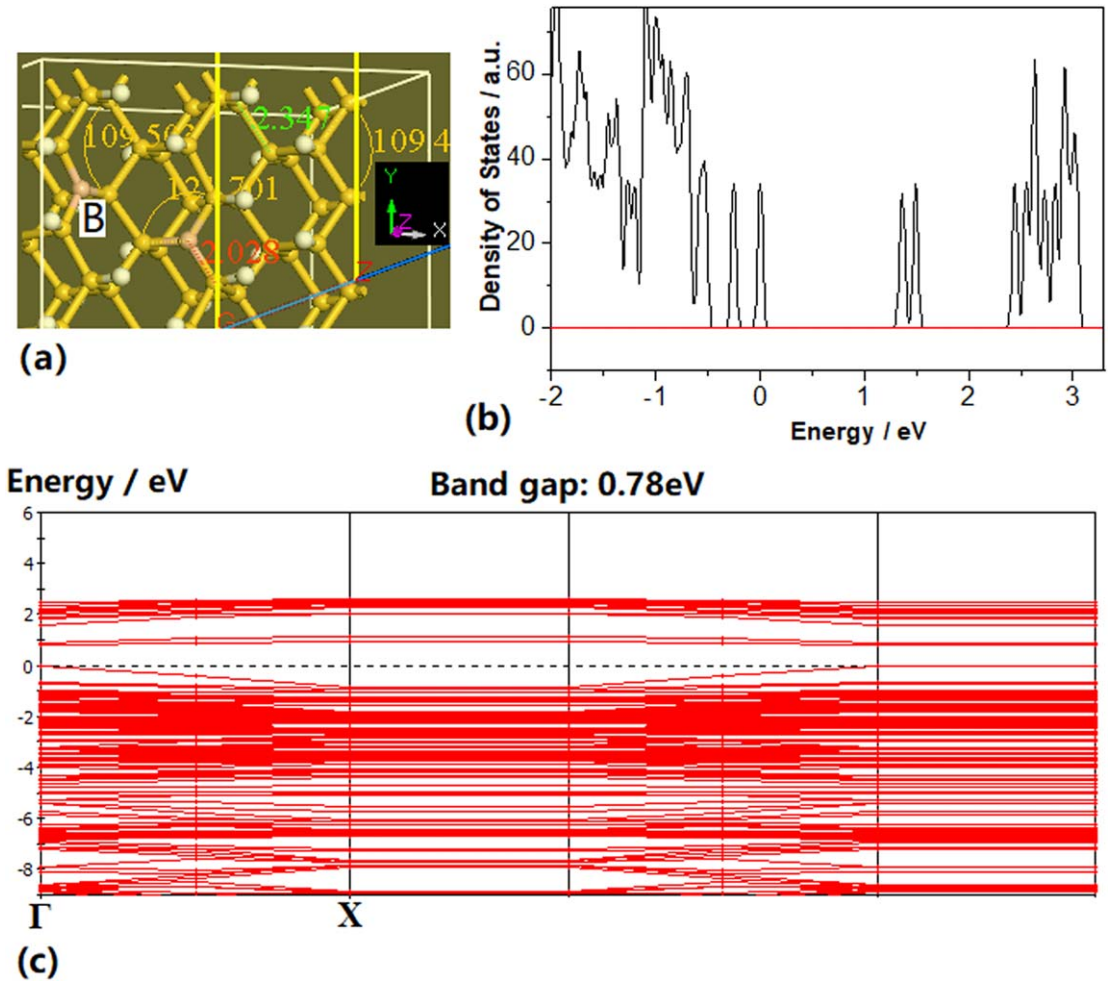

Figure 5. (a) A structure model of the Si_9 doped with boron (pink ball) built on surface, where the larger angle of Si–B–Si bond is about 122° occurring after the optimum process. (b) The density of states of the Si_9 doped with boron on surface, where the localized states occur near the valence band. (c) The energy band of the Si_9 doped with boron on surface, in which the narrower direct bandgap of 0.78 eV can be observed.

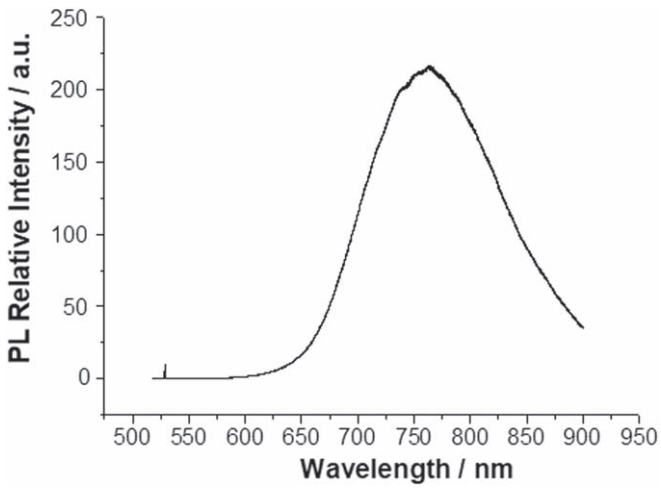

Figure 6. The emission peak in PL spectra on the sample of the pure Si_9 at room temperature, in which the light beam at 514 nm in Ar ion laser is focused on the samples for excitation.

the enhanced emission originated from the direct bandgap in the pure Si_9 has been observed in the PL measurement, in which a wider region of emission wavelength from 600 nm to 900 nm should have a good application for photovoltaic material in solar energy transformation.

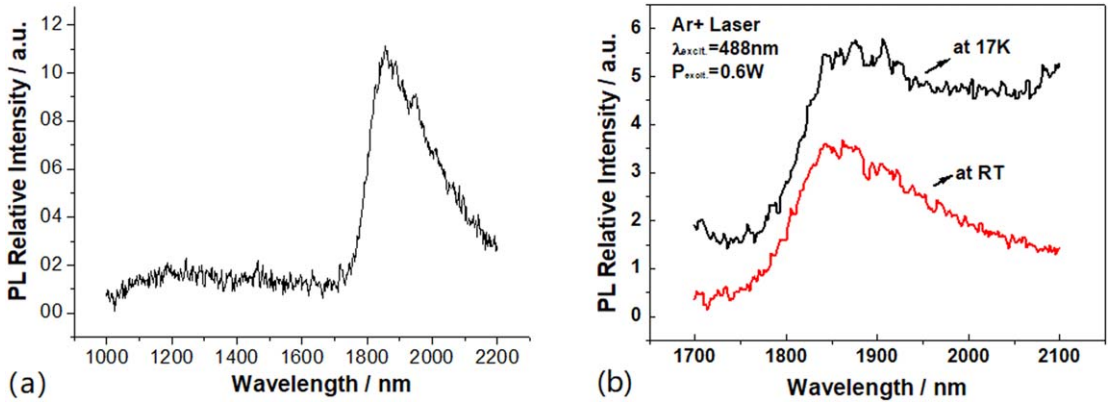

Figure 7. (a) The emission peak near 1850 nm observed in PL spectra at room temperature on the sample of the Si_9 doped with nitrogen on surface, in which the light beam at 488 nm in Ar ion laser with 0.6 W power is focused on the samples for excitation. (b) A comparison between the PL spectra at different temperature, where the PL spectrum in black curve is measured at 17 K and the PL spectrum in red curve is measured at room temperature.

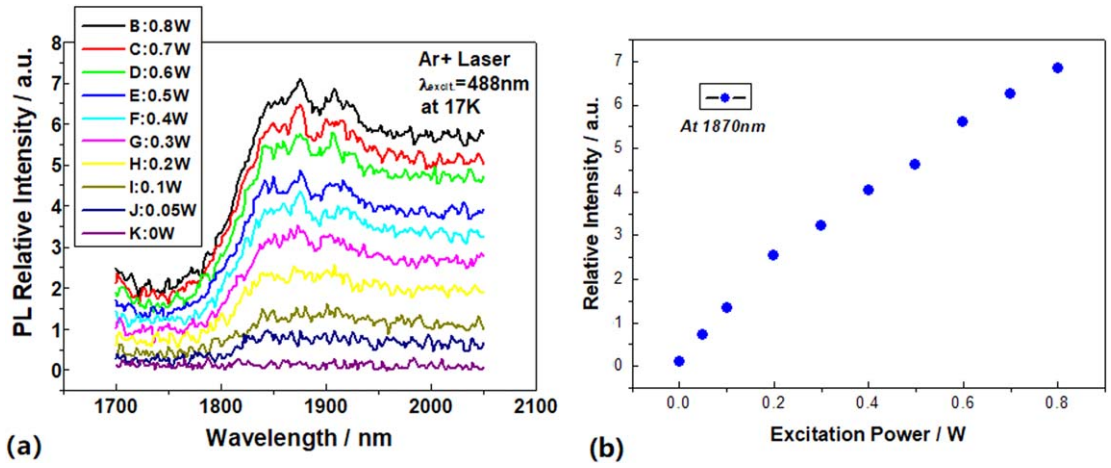

Figure 8. (a) The PL spectra on the sample of the Si_9 doped with nitrogen on surface, where the power curves at 17 K are obtained through changing the excitation power from 0.05 ~ 0.80 W in Ar ion laser at 488 nm. (b) The relative intensity evolution of the PL emission near 1870 nm on the Si_9 doped with nitrogen, possessing the emission characteristic of the optical material with direct bandgap.

On the sample of the Si_9 doped with nitrogen, the emission peak near 1850 nm has been observed in PL spectra at room temperature, whose wavelength region is wider from 1700 nm to 2200 nm, as shown in figure 7(a). It is interesting to make a comparison between the PL spectra at 17 K and at room temperature, as exhibited in figure 7(b). In the PL measurement experiment, the light beam at 488 nm in Ar ion laser is focused on the samples for excitation with 0.6 W power.

In the PL measurement on the sample of the Si_9 doped with nitrogen, the power curves at 17 K are obtained through changing the excitation power from 0.05 ~ 0.80 W in Ar ion laser at 488 nm, as shown in figure 8(a), in which the broader distribution in the wavelength region longer than 1800 nm may be originated from doping states of nitrogen. Its relative intensity evolution of the PL emission near 1870 nm, originated from the power curves in figure 8(a), is exhibited in figure 8(b), which has a near linear potential with power change. The experimental measurement with changing excitation power exhibits the emission characteristic on the optical material with direct bandgap.

5. Conclusion

In summary, the new structure of Si_9 with direct bandgap has been formed through the two-step synthesis methodology. The calculation and experimental results demonstrate the discovery of the structure of Si_9 with direct bandgap. The simulating calculation shows that the Si_9 structure, involving 9 silicon atoms in an unit, possesses the six-membered sp3 silicon rings shape and the direct bandgap is near 1.59 eV. The enhanced

emission near 780 nm originated from the direct bandgap of the Si_9 has been observed in the PL spectra at room temperature. It is discovered that the Si_9 can be easily doped as both p- and n-type on surface, such as the n-type Si_9 doped with nitrogen and the p-type Si_9 doped with boron, where the narrower direct bandgaps can be obtained. In the experimental measurement, the enhanced PL emission near 1850 nm originated from the narrower direct bandgap has been observed at 17 K on the Si_9 doped with nitrogen. These new characteristic on the structure of Si_9 with direct bandgap will make it become a next-generation semiconductor material for photovoltaic and optoelectronic technologies.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant No. 11847084).

Competing interests

The authors declare no competing financial interests and no-financial interests.

ORCID iDs

Wei-Qi Huang https://orcid.org/0000-0002-9591-8740

References

[1] Botti S, Flores-Livas J A, Amsler M, Goedecker S and Marques M A L 2012 Low-energy silicon allotropes with strong absorption in the visible for photovoltaic applications *Phys. Rev* **86** 121204
[2] Theis T N and Solomon P M 2010 It's time to reinvent the transistor *Science* **327** 1600–1
[3] Fujita M 2013 Silicon photonics: nanocavity brightens silicon *Nature Photon.* **7** 264–5
[4] Ngetal W L 2001 An efficient room-temperature silicon-based light-emitting diode *Nature* **410** 192–4
[5] Guleria A, Neogy S, Maurya D K and Adhikari S 2017 Si24: an efficient solar cell material *J. Phys. Chem.* C **121** 24302–16
[6] Kojima T, Sugimoto H and Fujii M 2018 Size-dependent photocatalytic activity of colloidal silicon quantum dot *J. Phys. Chem.* C **122** 1874–80
[7] Xiang H J, Huang B, Kan E, Wei S-H and Gong X G 2013 Towards direct-gap silicon phases by the inverse band structure design approach *Phys. Rev. Lett.* **110** 118702
[8] Shockley W and Queisser H J 1961 Detailed balance limit of efficiency of pn junction solar cells *J. Appl. Phys.* **32** 510–9
[9] Huang W-Q, Liu S-R, Huang Z-M, Wu X-K and Qin C-J 2017 Localized states and quantum effect of photo-generated carriers in photovoltaic system *Sci. Rep.* **7** 7221
[10] Duck Young Kim S S, Oleksandr O K and Timothy A S 2015 Synthesis of an open-framework allotrope of silicon *Nature Mat.* **14** 169–73
[11] Linghu J, Shen L, Yang M, Xu S and Feng Y P 2017 *J. Phys. Chem.* C **121** 15574–9
[12] Bryan J D and Stucky G D 2001 Eu4Ga8Ge16: a new four-coordinate clathrate network *Chem. Mater.* **13** 253–7
[13] Yamanaka S and Maekawa S 2006 Structural evolution of the binary system Ba-Si under high-pressure and high-temperature conditions *Z. Naturforsch.* **61b** 1493–9
[14] Wosylusetal A, Prots Y, Burkhardt U, Schnelle W, Schwarz U and Grin Y 2006 High-pressure synthesis of strontium hexasilicide *Z. Naturforsch.* **61b** 1485–92
[15] Wosylus A, Prots Y, Burkhardt U, Schnelle W and Schwarz U 2007 High-pressure synthesis of the electron-excess compound CaSi6 *Sci. Technol. Adv. Mater.* **8** 383–8
[16] Wosylusetal A, Prots Y, Burkhardt U, Schnelle W, Schwarz U and Grin Y 2006 Breaking the Zintl rule: high-pressure synthesis of binary EuSi6 and its ternary derivative $EuSi_{6-x}Gax$ ($0 \leqslant x \leqslant 0.6$) *Solid State Sci.* **8** 773–81
[17] Botti S, Flores-Livas J A, Amsler M, Goedecker S and Marques M A L 2012 Low-energy silicon allotropes with strong absorption in the visible for photovoltaic applications *Phys. Rev. B: Condens. Matter Mater. Phys.* **86** 121204
[18] Xiang H J, Huang B, Kan E, Wei S-H and Gong X G 2013 Towards direct-gap silicon phases by the inverse band structure design approach *Phys. Rev. Lett.* **110** 118702
[19] Wang Q, Xu B, Sun J, Liu H, Zhao Z, Yu D, Fan C and He J 2014 Direct band gap silicon allotropes *J. Am. Chem. Soc.* **136** 9826–9
[20] Lee I-H, Lee J, Oh Y J, Kim S and Chang K J 2014 Computational search for direct band gap silicon crystals *Phys. Rev. B: Condens. Matter Mater. Phys.* **90** 115209
[21] Amsler M, Botti S, Marques M A L, Lenosky T J and Goedecker S 2015 Low-density silicon allotropes for photovoltaic applications *Phys. Rev. B: Condens. Matter Mater. Phys.* **92** 014101