European Science Review 2024,
No 9–10.
ISSN 2310-5577

PREMIER Publishing
ppublishing.org

Section 4. Physics

DOI:10.29013/ESR-24-9.10-16-20

STUDY AND CALCULATION OF SULFUR- MANGANESE-SILICON CELL IN SILICON LATTICE

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Cite: *Utamuradova Sh. B., Mavlyanov A. Sh., Matchonov Kh. J. (2024). Study and Calculation of Sulfur-Manganese-Silicon Cell in Silicon Lattice. European Science Review 2024, No. 9–10.* https://doi.org/10.29013/ESR-24-9.10-16-20

Abstract

A model of hypothetical Si_2MnS structure similar to the cubic structure of F43m-β-MnS has been proposed and quantum-mechanically calculated. $E_g \approx 0.22$ eV energy gap of the Si_2MnS structure obtained in the course of quantum chemical numerical calculation of position of electrons and the level $E_i \approx 0.226$ eV revealed during the study of the photoconductivity of the Si< Mn,S >sample, have been analyzed and compared. According to the authors, further thorough theoretical studies, detailed quantum chemical calculations and experiments in the field of engineering a novel class of hybrid compounds with a cubic lattice of diamond type with the participation of elements of groups IV/III-V and IV/II-VI, could help forecast new structures.

Keywords: *model, quantum-mechanical calculation, non-isovalent compound, single crystal silicon, manganese, sulfur, photoconductivity, forbidden band, ionic and covalent bonds*

Over recently, the intentional formation of chemical complexes from a small number of defects with an ordered arrangement of impurity atoms and the atoms of thebasic material in the lattice with a partially ionic and partially covalent nature of bonds between them helpsimprove the functional parameters of semiconductor structures and thusvary their properties.

In particular, one of the promising areas is widening functional properties of single crystalline silicon with non-isovalent compounds in the crystal lattice with phases of the $Si_2A_{II}B_{VI}$ type, which represent a “hybrid” of the cubic lattice of silicon Si and sphalerite ZnS (cubic modification).

Theoretical studies, quantum chemical calculations and the experiments focused on engineering novel class of hybrid chemical complexes with a cubic diamond-structured lattice that consist of elements of groups IV/III–V and IV/II–VI, are conducted by researchers of leading universities and research centers around the world. In particular, in (Liying Jiang, Toshihiro Aoki, David J. Smith, Andrew V. G. Chizmeshya,

§ Jose Menendez, and John Kouvetakis, 2014; Joongoo Kang, Ji-Sang Park, Pauls Stradins, and Su-Huai Wei. 2017), the possibilities of nonequilibrium growth of complexes of Si-IV/III–V and Si-IV/II–VI -type compounds for receiving optically sensitive materials based on Si have been described. In (Liying Jiang, Toshihiro Aoki, David J. Smith, Andrew V. G. Chizmeshya,§ Jose Menendez, and John Kouvetakis, 2014; Joongoo Kang, Ji-Sang Park, Pauls Stradins, and Su-Huai Wei. 2017), the authors suggest that the "hybrid" phases of Si_2AlP (or Si_2ZnS) with lattice constants close to the lattice constant of the base matrix might be ideal materials with controlled local chemical order around Si atoms. In the above-mentioned studies, using the first-principles calculation methods, the authors discuss the influence of chemical order on the electronic and optical properties of non-isovalent solid solutions.

In this regard, this paper deals with modelling and quantum-mechanical calculation ofa hypothetical structure *Si_2MnS* (Fig. 1) which is similar to the cubic structure *F43m*-β-*MnS* (zinc blende).In doing this the authors have beenmotivated by a number of interesting studies donein this area.

In particular, in (Otrokov, M. M., Ernst, A., Tugushev, V. V., Ostanin, S., Buczek, P., Sandratskii, L. M., Fischer, G., Hergert, W., Mertig, I., Kuznetsov, V. M., and Chulkov, E. V., 2011) to model the Si*N*/Mn molecular alloy, the researchersapplied $(N+1)$–layerthick tetragonal supercells, composed of *N* monolayers of Si and one Mn molecular layer. The three different Mn configurations were considered, i.e. the substitutional site MnS (1), interstitial site MnI (2), and the configuration, labeled as IS (3), where Mn atoms occupy both interstitial and substitutional positions.

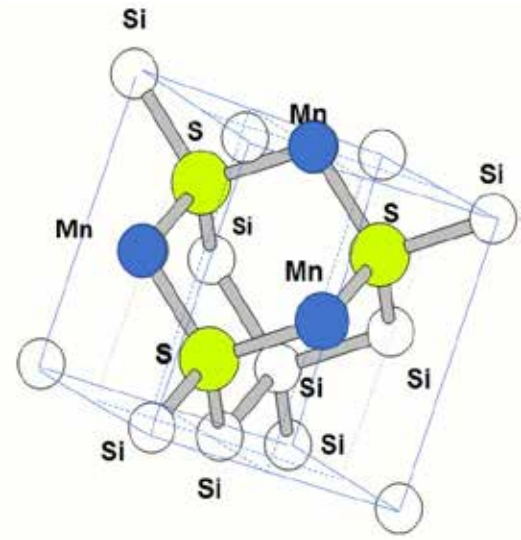
The Si thickness has varied between 7 and 31 monolayers. The unit cell vectors **a**, **b**, and **c** were directed along [110], [110], and [001], respectively, with $\overline{a} = b = a_{Si}/\sqrt{2}$ and $c = a_{Si(N+1)}/4$, where a_{Si} = 5.46 A is the equilibrium lattice parameter of Si.

For the structural relaxation in (Otrokov, M. M., Ernst, A., Tugushev, V. V., Ostanin, S., Buczek, P., Sandratskii, L. M., Fischer, G., Hergert, W., Mertig, I., Kuznetsov, V. M., and Chulkov, E. V., 2011), the authors used the Vienna *ab initio* Simulation Package (VASP) 49–51 within the generalized gradient approximation to exchange-correlation potential.

The electron-ion interactions were described by projectoraugmented wave pseudopotentials, and the electronic wavefunctions were represented by plane waves with a cutoff energyof 500 eV.

In this work, the authors investigated how magnetic properties of the concerned material affects the structural properties of such solutions. After optimization, the authors identified a shift in the positions of Mn atoms in three configurations, which changed the structural properties of the material. When studying the magnetic properties, exchange interactions were also taken into account. Spin-polarized densities of electron states were calculated for three configurations.

Figure 1. *Cubic F43m – β – MnS (zinc blende)-type hypothetical structure of Si_2MnS*



In this regard, as noted above, we have chosen the cubic F43*m* – *β* –MnS (zinc blende)-type hypothetical structure of Si_2MnS (Fig. 1) for further modeling and quantum-mechanical calculations.

An isolated Mn atom in Si matrix mainly occupies a tetrahedral interstitial position in the Si lattice acting as a donor and thus becoming a positively charged ion, while if the Mn atom occupies a substitutional position it acts as an acceptor thus becoming a negatively charged ion. The situation in the Si: Mn dilute alloys is, however, more complex. These materials attracted moreinterest after the observation of a ferromagnetic (FM) state with high Curie temperature of about 400 K (Otrokov, M.M., Ernst, A., Tugushev, V.V., Ostanin, S., Buczek, P., Sandratskii, L.M., Fischer, G., Hergert, W., Mertig, I., Kuznetsov, V.M., and Chulkov, E.V., 2011).

Detailed x-ray and magnetic studies of Si: Mn dilute alloys with low and moderate (from 0.5 to 17.5 at. %) Mn content indicated that, possibly due to extremely difficult doping control process, these systems tend to be in very inhomogeneous state, and the Mn ions enter not only substitutional or interstitial positions of the Si lattice but also could form molecular clusters and precipitates (Otrokov, M.M., Ernst, A., Tugushev, V.V., Ostanin, S., Buczek, P., Sandratskii, L.M., Fischer, G., Hergert, W., Mertig, I., Kuznetsov, V.M., and Chulkov, E.V., 2011).

Sulfur, in turn, as an element of group VI of the periodic table, occupying asubstitution position, participates in the formation of *sp3*-hybrid bonds with four nearby silicon atoms. In this case, the remaining two excess electrons introduce two donor levels into the forbidden band of silicon.

Thus, and owing to:

- the presence in of the cubic structure of F43*m*–*β*–*MnS* (zinc blende) similar to the cubic structure of diamond-type silicon;
- the existing experimental facts confirming cases of substitution of Mn and S atoms for Si crystal structure sites;
- the availability of the computing processing power and quantum-mechanical apparatus;
- the fact of ever improving methods for controlling doping processes whereby appears a real chance to exactly specify the position of an impurity atom with a highly predictable probability (especially since effective methods for controlling the alloying process have been developed recently by using the so-called δ-alloying method (Harris, J.J., 1993; Nazmul, A.M., Amemiya, T., Shuto, Y., Sugahara, S., and Tanaka, M., 2005), when the position of the impurity is confined on the length scale corresponding to the lattice constant, and is thus placed into the base matrix of Si) all the above-mentioned pre-conditions make it possibleto theoreticallymodel, calculate such structures, perform experimental doping of silicon with manganese and sulfur impurities, compare experimental data with quantum mechanical calculation results, and afterwardsforecastsimilar structures in the future.

The calculations were performed using and thanks to free software Abinit, designed for calculations applying the density functional method, the Firefly Quantum Chemistry License Package and the freely distributed visualizer programs ViewMol3D and Molekel.

Using the available quantum-chemical and molecular-dynamic methods, a diamond lattice cell of Si with four surrounding atoms located at the vertices of a regular tetrahedron inside a cube, as well as a diamond-type crystal lattice structure, were constructed. The corresponding lattice parameters a = =5.43095Å,d(A–B)=2.35167Å,andd(A–A)= = 33.84026 Å were set for Si.

The numerical calculation revealed noticeable changes in the charge state and the electrostatic potential of the Si matrix with Si_2MnS cells compared to the base Si lattice. Mn atoms in substitutional positions acquire a negative charge, whereas S atoms in substitutional positions acquire a positive charge, resulting in an ionic component of the interatomic bond, which confirms the theory of a *"partially ionicand partially covalent"* components of the bond in binary compounds in the basic matrix of Si. The electronic spectrum of the Si_2MnS structure with absorption peaks corresponding to transition energies of 2.65 eV, 2.39 eV, 2.28 eV, 2 eV, 1.8

eV and 1.01 eV were also revealed by calculations. The results of numerical calculation of the position of valence electrons of the Si_2MnS structure revealed the gap value E_g = = 0.22 eV, which is confirmed by the presence of the highest occupied orbital HOMO with a value of 0.1431 eV and the lowest unoccupied orbital LOMO with a value of 0.0811 eV, respectively.

In parallel, dopingof Si with sulfur and manganese by using diffusion doping technique in vacuumed (10–4 bar) and sealed quartz ampoules at a temperature of 1260 °C and 1200 °C, respectively, was carried out for a duration that would be sufficient for ensuring uniform doping. Theinitial samples were Si doped with boron, with an initial specific resistance in the range of ρ = 1 Ω cm. After doping with Mn and S, the initial silicon remained of *p*-type, but the resistivity increased to $\rho = 2.4 \times 10^4$ Ω cm.

In order to study the photoconductivity (PC) curve of the silicon sample doped with Mn and S, the PC measurements have been done at IKS (infrared diapason)-21 – type spectrometer equipped with a cryostat, which allows to study photoconductivity in a wide temperature range (T = 77 ÷ 350 K). To study the impurity photoconductivity only, a double filter of polished monocrystalline silicon wafer was used, which was installed before the cryostat window after the infrared light emitter of IKS-21.

Photoconductivity in silicon samples doped with Mn and S in the dark launches at $h\nu \approx 0.226$eV. In the range of $h\nu = 0.226–0.42$eV, with an increase in the photon energy, the photoconductivity increases continuously and then the saturation region of the photocurrent gradually begins to manifest itself. At $h\nu$ = 0.42 eV, a sharp decrease in photoconductivity occurs, and a further increase in the photon energy leads to a noticeable decrease in photoconductivity value with a relatively deep minimum at $h\nu \approx 0.45–0.46$ eV.

In view of the above mentioned it could be stated that the quantum-chemically calculated gap value, i.e. $Eg = |–LOMO–HOMO| \approx$ ≈ 0.22eV of the Si_2MnS structure, with a certain degree of consent, is confirmed by the appearance of the level $Ei \approx 0.226$ eV revealed in the course of study of photoconductivity of the Si<Mn, S> sample (Mavlyanov, A. Sh., Aminov, N. Sh., Sultanova, Yu. A., Khujaniyazova, A., 2019), which is most probably associated with the excited transition of an electron from an impurity level to the conduction band.

Conclusion

According to the authors, any further in-depth theoretical studies, the detailed quantum-chemical calculations and more thoroughly performed experiments in the field of engineering a new class of hybrid compounds with a cubic lattice of the diamond type where the elements of groups IV/III–V and IV/II–VI are embedded in Si matrix, will make it possible to forecast novel crystal structures in the future.

Meanwhile, experimental study of the structural and electrophysical properties of such materials on single-crystal silicon doped with impurity atoms hypothetically forming Si-IV/III–V and Si-IV/II–VI-type compounds would contribute to the expansion of the parameters of single-crystal silicon and could shed light on the possibility of engineering silicon materials with close coordinates of absolute minima in momentum space. In this case, it is necessary to take into account the fact that the electronic properties of such structures will differ depending on the ordered and random arrangement of impurity atoms in the silicon lattice.

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submitted 04.10.2024;
accepted for publication 24.10.2024;
published 26.11.2024

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