On the role of induced impurity potential of $\beta$-FeSi$_2$

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Abstract

We have examined the roles of induced impurity potential into $\beta$-FeSi$_2$ lattice. Because of the specific band structure, new mechanism through the induced impurity potential are essential for the improvement of optical properties. Expecting the role of induced impurity potential as the source of exciton, we try to apply the successful case of GaP:N to the $\beta$-FeSi$_2$. If C atom is substitutionally dissolved in the $\beta$-FeSi$_2$ lattice, impurity potential caused by local C atom would generate bound exciton because of the difference of electronegativity between Si and C atoms. The oscillator strength would be expected to be greatly enhanced without any help of phonon because of the formation of Wanier exciton around C with relatively small radius.

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1. Introduction

The role of induced impurity potential on the optical properties of $\beta$-FeSi$_2$ has not been completely understood until now. Concerning the photoluminescence (PL) properties, it is observed that Al doped $\beta$-FeSi$_2$ shows the enhancement of PL intensity[1]. Based on their article, the Al doping by ion implantation results in the decrease in Si vacancies, which leads to the enhancement of PL intensity. On the other hand, ion beam synthesized (IBS) $\beta$-FeSi$_2$ devices newly fabricated by dislocation engineering method shows decrease in electroluminescence (EL) intensity at room temperature is relatively restrained[2]. In contrast, thermal quenching drastically decreases the EL intensity at room temperature as already found in the conventional IBS $\beta$-FeSi$_2$ devices[3]. Considering the both experimental cases, the impurity potential induced into $\beta$-FeSi$_2$ lattice probably plays an important roles on determination of various optical properties. In this article, we, therefore, investigate induced impurity potential from the viewpoints of theory and the numerical calculation and propose the new method to improve the optical properties.

2. Theory and Calculations

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Iron-dicilicide $\beta$-FeSi$_2$ has a complex crystalline structure composed of 16 iron atoms and 32 silicon atoms per unit cell [4]. Concerning the electronic states reflected by such a complex crystalline structure, various calculations such as APW [5], LMTO with LDA[6,7] the semiempirical tight-binding [8] and FLAPW[9] methods suggest the rather structure sensitiveness for the lowest gap in $\beta$-FeSi$_2$. The self-consistent LMTO in its scalar relativistic version within the LDA scheme including exchange and correlation effects shows the presence of two energetically close valleys in the conduction band whereas there exists only one summit, i.e., $\Lambda$ point between $\Gamma$-$Z$ in the Brillouin zone, in the valence band [10]. Based on this article, one of two valleys locates at $\Lambda$ point and another at Y point. Also, the calculation results by A.B.Filonov et al[7] show the presence of the same two valleys in the conduction band ($\Lambda$ and Y points) whereas two summits appear in the valence band: one at $\Lambda$ point and another at Y point although calculated energy dispersion is very similar to Lange’s result[10] with showing slightly higher energy level at Y point. The calculations by Christensen[6] suggest the possibility of indirect gap, but there only exists slight difference between direct and indirect gap.

From the experimental viewpoint, it is also difficult to determine whether dominant transition process is direct or indirect. Indirect energy gap accompanying with direct gap locating at only a few tens meV above is observed[11-13] whereas only a direct band gap is observed by other groups[14-16]. Furthermore, changes in the lattice parameter is turned out to have the influence on band structure with the result that the direct and indirect transition energies somewhat change[17].

As stated above, we can conclude the dominant transition process between bands are strongly ascribed to the structure sensitiveness of lattice on the basis of the results of theories and experiments. Especially differences of energy levels between two valleys in conduction band and between $\Lambda$ and Y points in the valence band are very close less than 0.1eV, which can be easily changeable by the fabrication methods and calculation ways such as APW,LAPW and LMTO etc with resulting in the appearances of the direct or indirect band gaps. Furthermore, considering the specific band structure of $\beta$-FeSi$_2$ as described above, lattice vibrations would play important role on determination of transition processes although phonon energy is very small in comparison with Fermi level. Consequently, we consider that it is essential to introduce impurity potential into this lattice for the purpose of improving the optical properties of $\beta$-FeSi$_2$.

For example, FeSi$_2$ devices newly fabricated by dislocation engineering method exhibits improvement for the optical properties[2]. In this case, we can consider the presence of strain field $V(r)$ around the dislocation; thus impurity potential $H'$ can be given in the following manner:

$$ H' = \sum_{k,k'} V_{kk'} \hat{\psi}^{\dagger}_{k} \hat{\psi}^{\dagger}_{k'} $$

(1)

$$ V_{kk'} = \int \tilde{V}_k(r) V(r) \psi_k(r) d^3r $$

where $\hat{\psi}^{\dagger}_{k}$ and $\hat{\psi}^{\dagger}_{k'}$ are creation and annihilation operators of a conduction electron with momentum $k$ and $k'$ and $\psi_k(r)$ is the wave function with momentum $k$ of Bloch electron. If we assume $V_{kk'} = V_{kk'} =$const, then the Hamiltonian $H$ including the above impurity potential $\hat{H}'$ can be easily diagonalized.

$$ H = \sum_{k,k'} (E_k \delta_{kk'} + V_0) \hat{\psi}^{\dagger}_{k} \hat{\psi}^{\dagger}_{k'} = \sum_{k} E^{(k)} \hat{\psi}^{\dagger}_{k} \hat{\psi}_{k} $$

(2)

where

$$ \tilde{C}_{k} = \sum_{\eta} \Gamma_{k\eta} \hat{\psi}_{\eta}^{\dagger} $$

Above equation shows that $E^{(k)}$ is an eigen value for the newly formed state $k$, which is bound by the presence of impurity potential. From simple numerical calculation, impurity level is formed at the top of energy level when $V_0 > 0$. In contrast, lowest energy level corresponds to impurity state for the case of $V_0 < 0$. Fig 1 schematically summarizes the numerical calculation results for $E^{(k)}$.

When dislocation is formed(or introduced) in the $\beta$-FeSi$_2$ lattice, electronic charge distribution in the area close to dislocation is somewhat different from the rest of lattice because of the local disarrangement of atomic configuration caused from dislocation. Consequently such a distortion of charge around the dislocation forms local potential, i.e., strain field $V(r)$, which is attractive or repulsive to the conduction electrons, with depending on the sign of $V_0$: attractive interaction for $V_0 < 0$ while repulsive interaction for $V_0 > 0$. Provided attractive interaction
works between electron and strain field, excitons would be formed around dislocation; thus the improvement of optical properties would be somewhat related to this formation of exciton.

Next let us consider the other case, that is, the role of dopant. Concerning the photoluminescence (PL) properties, Al doped $\beta$-FeSi$_2$ shows the enhancement of PL intensity[1]; thus doping is very effective measure to improve the optical properties. However the detailed role of doping element in $\beta$-FeSi$_2$ lattice hasn’t been well-understood. As stated above, dominant transition process between bands can be easily changeable, so we can not expect phonon assisted transition process (indirect process) because of too weak oscillator strength. Instead, we can expect the impurity-bound excitons such as the case of isoelectronic doping of GaP:N. When nitrogen is substitutionally dissolved in the GaP lattice[18], higher electronegativity of N(3.04 Pauling electronegativity) can therefore attract the electrons with forming a bound Wannier exciton having the radius of about 3nm. It should be noted that this exciton radius is very small in comparison with the usually observed exciton’s radius of about 10nm. Such a small radius means that this Wannier exciton can possible have any wave vector in the 1st. B.Z. from the demand of the uncertainty principle as shown below,

$$\Delta r \cdot \Delta k > \hbar$$

Accordingly oscillator strength is greatly enhanced without any help of phonon because the electron trapped around N, the energy level of which locates at somewhat below the X point at the conduction band, has a long range of momentum. Then let us apply the above idea to the improvement of optical properties of $\beta$-FeSi$_2$. We can mention the carbon as the possible candidate element for isoelectronic doping because Pauling electronegativity of C is 2.55 while that of Si is 1.90. Furthermore, based on the many experimental results, it is well-known that small atom such as N or O can easily generate bound state. Although radiuses of O and N are about 55 and 60 pm, respectively and are somewhat smaller than that of C atom (about 77pm), C atom seems to be sufficient candidate considering the atomic radius of Si being about 118pm. If C atom is substitutionally dissolved in the $\beta$-FeSi$_2$ lattice, C atom probably attracts electrons because of higher electronegativity than that of Si; thus we can expect larger negative charge of carbon than that of Si.

For the purpose of examining the charge of carbon which occupies Si site in the $\beta$-FeSi$_2$ lattice, we calculate the charges for CFe$_{15}$Si$_{29}$ and Fe$_{15}$Si$_{30}$ clusters, where the latter cluster, i.e., Fe$_{15}$Si$_{30}$ cluster is used for the comparison with charge of C atom. The center of latter cluster is Si atom and CFe$_{15}$Si$_{29}$ cluster is obtained by exchange of C atom into Si atom which occupies the center of Fe$_{15}$Si$_{30}$ cluster; thus atomic configurations of both cluster are same except for the center atom. When constructing the clusters, we assume each cluster includes all atoms within the distance from the center =0.51nm. Figure 2 shows CFe$_{15}$Si$_{29}$ cluster used for calculations. To calculate accurate charge, we perform DFT calculation using Gaussian 03 program[19] with basis set of 6-31G(d). Estimated charges on the basis of Mulliken population analysis are -0.93 for C atom and -0.83 for Si atom center of cluster. Numerical calculation confirms that C atom attracts more electrons than Si atom because of high electronegativity; thus the formation of bound Wannier exciton with radius of a few nm could be expected. Furthermore if energy level of electron trapped around C atom is somewhat less than two valleys in the conduction band of $\beta$-FeSi$_2$ lattice, then oscillator strength is expected to be greatly enhanced without any help of phonon, that is, no occurrence of drastic decreases in oscillator strength due to thermal quenching. However detailed studies
including precise calculations mainly related to the energy level of impurity atom are much required to improve the optical properties with an emphasis on the formation of Wannier exciton.

3. Conclusions

We have examined the roles of induced impurity potential into $\beta$-FeSi$_2$ lattice. First, many experiments and theoretical calculations suggest that it is very difficult to determine which transition process is dominant, direct or indirect. Because of the specific band structure, new mechanism through the induced impurity potential are needed for the improvement of optical properties. The role of dislocation can be, therefore, regarded as the introduction of impurity level caused by the strain field around dislocation, which would probably form weakly bound excitons with resulting in the improvement of optical properties. Secondly, considering the isoelectronic doping, we apply the successful case of GaP:N to the $\beta$-FeSi$_2$. If carbon atom is substitutionally dissolved in the $\beta$-FeSi$_2$ lattice, the oscillator strength would be expected to be greatly enhanced without any help of phonon because of the formation of Wannier exciton around C.

References

[1] Y. Terai, Y. Maeda and Y. Fujiwara, Physica B376-377 (2006) 799-802
[2] M.A.Lourenço, R.M.Gwilliam, G.Shao and K.P.Homewood, Nucl.Instr. and Meth.in Phys.Res. B206(2003)436.
[3] M.A.Lourenço, T.M.Butter, A.K.Kewell, R.M.Gwilliam, K.J.Kirby and K.P.Homewood, Jpn.J.Appl. Phys.40(2001)4041.
[4] P.Y.Dusausoy, J.Protas, E.Wandji and B.Roques, Acta Cryst. B27(1971)1209.
[5] J.Eppenga, J.Appl.Phys. 68(1990)3027
[6] N.E.Christensen,Phys.Rev. B42(1990)7148.
[7] A.B.Filonov, D.B.Migas, V.L.Shaposhimikov, N.N.Dorozhkin, G.V.Petrov, V.E.Borisenko, W.henrion and H.Lange, J.Appl.Phys. 79(1996)7708.
[8] L.Migli and G.Malegori, Phys.Rev. B52(1995)1448.
[9] S.Isebitt, J-E.Rubensson, M.Nicodemus, T.Böske, S.Blügel, W.Eberhardt, K.Radermarcher, S.Mantl and G.Bihlmayer, Phys.Rev. B50(1994)18330.
[10] H.Lange, Thin Solid Films 381(2001)171.
[11] W.Henrion, St.Brehme, I.Sieber, H.von Känel, Y.Tomm and H.Lange, Solid State Phenom. 51(1996)341
[12] K.Takakura, N.Hiroi, T.Tsunemasa, S.Chichibu and F.Hasegawa, Appl.Phys.Lett. 80(2002)556.
[13] H.Udono and I.Kikuma, Jpn.J.Appl.Phys., Part 1(2002)L583.
[14] H.Kakemoto Y.Makita, S.Sakuragi and T.Tsukamoto, Jpn. J. Appl.Phys., Part 1 38(1999)5192
[15] M.Ožvold, P.Mraško and V.Gašparik, Czech.J.Phys.50(2000)677...
[16] S.Chu, T.Hirohada and H.Kan, Jpn.J.Appl.Phys., Part 2 41(2002)L229
[17] S.J.Clark, H.M-Al.Allak, S.Brand and R.A.Abram, Phys.Rev.B 58(1998)10389.
[18] D.G.Thomas and J.J.Hopfield, hyd.Res.150(1966)680.
[19] Gaussian 03, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Izmaylov, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D.Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefano, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. W. M. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pope, Gaussian, Inc., Wallingford CT, 2004.