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Theoretical Studies on the Realistic Low Concentration Doping in Silicon Semiconductors by Accelerated Quantum Chemical Molecular Dynamics Method

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1. Introduction

Recently, computational chemistry has made great impacts on the silicon semiconductor technology and processing. Especially, first-principles calculation is known to be a most powerful tool to clarify the band structure, doping level, surface reaction processes, crystal growth processes and so on in the silicon and its related materials. However, the first-principles calculation requests huge computational costs and then only a small model including 50~100 atoms can be simulated. The above defect of the first-principles calculation leads to a lot of problems to design new silicon devices and processes. For example, although the dopant concentration of the silicon wafer is regularly less than 0.1 %, only the high concentration system of the dopants can be simulated by the first-principles approach, which leads to the misunderstanding of the band structures and doping levels. Moreover, the electronic states calculation of the hetero-interface in the source-drain-gate-channel system is also very difficult because it requires a large simulation model. Moreover, the effect of the grain boundary on the electronic states of the silicon semiconductor also cannot be simulated.

In order to solve the above problems, recently we have developed a new quantum chemical molecular dynamics program "Colors" [1,2]. Since this program is more than 5,000 times faster than the regular first-principles molecular dynamics program, a large simulation model including more than $200 \sim 1000$ atoms can be calculated. This is a significant merit compared to the regular first-principles program. It can solve the low-concentration problem of the dopants, interface electronic states problem, and grain boundary electronic states problem.

Hence, in the present study, we applied our accelerated quantum chemical molecular dynamics

program to the band structure calculation of the realistic low concentration doping model in the silicon semiconductor. Since the above calculation can not be performed by other simulation programs, this work is the first realistic result on the electronic states of the n-type and p-type silicon semiconductor.

Moreover, the electronic states dynamics of the silicon semiconductors are also simulated by the above new simulation software.

2. Theoretical Method

In the present study, we employed our accelerated quantum chemical molecular dynamics program "Colors" based on our original tight-binding theory [1,2]. In order to decrease the calculation time, some parameters such as ionization potential, zeta value of Slater-type orbital, resonance integrals, two-center electron-repulsion integrals, and exchange-repulsion integrals, are used.

3. Results and Discussion

Figure 1 shows three different calculation models. (a) pure silicon, (b) B-doped p-type silicon, and (c) P-doped n-type silicon. Model (a) constitutes of 216 Si atoms and one silicon atom is replaced by the B and P atoms in the models (b) and (c), respectively. Therefore, the doping concentration is equal to 0.46% in our realistic model. This concentration is much lower than those of the previous first-principles calculation studies. Figure 2 shows the density of states (DOS) of the above three models. The obtained band gap of the pure silicon is 1.17 eV, which is in good agreement with the experimental value of 1.13 eV. Regular first-principles calculations based on the density functional theory gives significant small band gap compared to the experimental results. We confirmed that our simulation program produces surprisingly appropriate band gap value compatible to the experimental results.

In the B-doped p-type silicon, the acceptor level appears at 0.030 eV above the valence band, which is also in agreement with the experimental value of 0.045 eV. In the P-doped n-type silicon, the donor level appears at 0.030 eV below the conduction band, which is also in good agreement with the experimental value of 0.045 eV. When we consider that the first-principles calculation based on the density functional theory cannot give the correct band gap value, we strongly insist that our quantum chemical molecular dynamics program has much accuracy for band gap calculation.

We also performed the dynamics simulation of the dopants in the silicon semiconductors and analyzed the change in the dopant levels depending on the time. All simulations were performed for 200 steps with a time step of 0.1 fs at 300 K, under the periodic boundary condition. Figure 3 shows the electronic states dynamics of the molecular orbital of the impurity level in the B-doped p-type silicon. From this figure, we observed the change of the molecular orbital during the simulation. Same phenomenon was observed in the P-doped n-type silicon. These results suggest that our original quantum chemical molecular dynamics program can analyze not only the band structure of realistic low concentration doping model, but also the electronic dynamics in the silicon states semiconductors.

4. Summary

We succeeded to analyze the band structure of silicon semiconductors including n-type and p-type materials, using realistic low concentration doping models. These results are in good agreement with the experimental results. When we consider that the first-principles calculation based on the density functional theory cannot give the correct band gap



Fig. 1 Calculation models (a) Pure silicon, (b) B-doped p-type silicon and (c) P-doped n-type silicon

value, we strongly insist that our quantum chemical molecular dynamics program has much accuracy for band gap calculation.

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Fig. 2 DOS of (a) pure silicon, (b) p-type Si and (c) n-type Si



Fig. 3 Electronic states dynamics of the molecular orbital of the impurity level in the B-doped p-type silicon