

Theoretical Study on the Microscopic Structure and Hydrogen  
Decoration of the Multivacancy in Crystalline Silicon

Toru AKIYAMA

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# Abstract

Vacancies in semiconductors are introduced in fabrication processes of semiconductor devices, and crucially affect the properties of host materials. Many efforts thus have been done to clarify the properties of vacancies. In silicon, structural and electronic properties of the monovacancy and the divacancy are well identified from many experimental and theoretical studies. However, the identification of vacancy aggregates (multivacancies) is less pursued compared with that of the monovacancy and the divacancy. Since multivacancies can be regarded as negative clusters within the crystal, it is highly likely that the negative clusters have stable sizes and structures (magic numbers) similar to ordinary clusters and peculiar features of the electronic structure can be found in these negative clusters. Theoretical investigation shows that there are several magic number multivacancies. Yet the distortion of surrounding atoms and electronic structures are not clarified. Furthermore, the structures of multivacancy-impurity complex such as hydrogen decorated multivacancies observed in Raman scattering experiments are also unidentified. In this thesis, we reveal the stable structures and the electronic structures of the multivacancy in crystalline Si based on the total-energy electronic-structure calculations within density functional theory. In addition, we clarify the stable structures and the vibrational properties of hydrogen (one of the most common and important impurities in Si) decorated multivacancies.

First, we investigate the stable sizes, the stable structures, and the electronic structures of the multivacancy. It is found that the stable multivacancies are hexavacancy  $V_6$  and decavacancy  $V_{10}$  within the accuracy of density functional theory. It is confirmed that the stability of the multivacancy is intuitively understood by concept of dangling bond counting, although the formation energies of multivacancies are drastically decreased by lattice relaxation which is not taken into account in the dangling bond counting model. The peculiar features of the electronic structures for the stable multivacancies are also revealed in the present calculation.

Next, we study the electronic structure of stable multivacancy  $V_{10}$  taken into account polarization of electron spin. It is found that electron spin is polarized due to substantial separation of dangling bonds generated by  $V_{10}$  and that the energy gain due to spin polarization is much larger than the gain of symmetry lowering distortion. The possibility of  $V_{10}$  as an electron trapping center is also investigated. Electrons can be trapped depending on the position of the fermi level and the *negative- $U$*  character in this system is found in the

present study.

Finally, we investigate the stable structures of hydrogen decorated multivacancies. Hydrogen atoms in multivacancies terminate dangling bonds, and then the multivacancies become completely decorated with hydrogen atoms. Furthermore, an  $H_2$  is capable of incorporated in the hydrogen decorated multivacancies. We perform calculations of vibrational frequencies of  $H_2$  molecule and Si-H bond in the multivacancy, on hydrogenated surface, and in hydrogenated internal surfaces (platelets). We then explain recent infrared absorption and Raman scattering experiments. The microscopic identification of  $H_2$  in the multivacancy is carried out from comparison of the theoretical results with experiments.