

## Evaluation of doctoral thesis

**Title: Nanostructures for solar cells: controlling the surface electronic properties by monolayers of carborane molecules**

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The main topic of the presented doctoral thesis is the study of self-assembled monolayers of carboranedithiols on the silicon surface using ab initio calculations based on the principle of density functional theory (DFT). Emphasis is placed on the possibility of non-invasive surface doping of monocrystalline silicon with regard to use in solar cells. This research is particularly relevant today, given the rising significance of renewable energy sources.

The initial chapter appropriately introduces the entire issue from a more general description of photovoltaics, its current and future share in global energy production, the influence on the decarbonization of the entire energy economy, through the rediscovered importance of monocrystalline silicon, and the fabrication technology of suitable and efficient p-n junctions, where special attention is paid to surface transfer doping (STD) consisting of charge transfer induced by adsorption of molecules with a large intrinsic dipole moment. Although the work is more of a theoretical and computational nature, I really appreciate the inclusion of these broader practical contexts and the overall overview.

The second chapter clearly describes the DFT theoretical background. Mainly, the individual contributions of the functional are appropriately discussed and explained. Considering that the exchange-correlation functional with the van der Waals interaction was used in the performed calculations, I highly value a more detailed explanation of this interaction compared to simple LDA, or just pure GGA approximations. The conclusion of the chapter also mentions the implementation details of SIESTA software used for the calculations utilizing the basis set of localized atomic orbitals, which is an advantageous solution for the mentioned problem.

The calculations of separate systems of gold, silicon, and carboranedithiol presented in the third chapter are a certain preparation for the actual problem. For both gold and silicon, the surface in the (111) direction is analyzed in more detail. Moreover, the surface reconstruction and hydrogen passivation of silicon surfaces are studied, which is directly related to the adhesion of carboranedithiols on these planes. Here, I consider it commendable that selected calculated parameters (e.g. lattice constants, energy band gaps, etc.) are compared with actual experimental results (not against other theoretical results as is the custom today) achieved on these systems, and the deviations are being explained in context of theory assumptions.

In a similar sense, to achieve a truly valid comparison of the experiment with theoretical results, the testing calculations of carboranedithiols on gold are performed in the fourth chapter, since more experimental work is available for this system. Furthermore, the procedures for transformation of the DFT accessible quantities to experimentally better available quantities (e.g. the change in the surface potential, work function, dipole moment, and charge density distribution near the surface) are presented here. This subsequent processing of the results gives a solid basis for the real usability of the entire work.

After this very thorough preparation, in the fifth final chapter comes the study of a new original system of carboranedithiols on silicon, which has not been experimentally studied so far. Here, energetically stable conformations A, B, and C are found. The A, C exhibit a chemisorption binding and B a physisorption binding. In both chemisorption bindings, the orientation of the molecular dipole is opposite, which results in opposite changes in the surface potential, a different silicon surface doping rate, but the same type of doping, which is interesting and surprising at the same time. In the case of experimental confirmation, the usefulness of DFT methods in predicting new electronic properties would again be demonstrated here. For the preparation of the mentioned monolayers on silicon, the computed energy balance of individual chemical reactions leading to carboranedithiol adsorption is helpful. In addition, the calculated dependence of force on the silicon-carboranedithiol displacement is interesting for the stability of the molecular layer against mechanical wear. Related to all incorporated details, the calculations are exhaustive, giving an almost complete picture of carboranedithiol behavior on the silicon surface.

Overall, the dissertation work is very honestly and comprehensibly processed. All achieved results stand on a solid foundation of careful preparation, are supported by high-quality analysis, and are appropriately interpreted. The last chapter contains scientifically original and up-to-date results with great application potential, not only in the field of solar cells but also in other electronic devices. The dissertation thus demonstrates the author's prerequisites for independent creative work and I definitely recommend it for defense.

Defense questions:

1. The carboranedithiol system on silicon has not been significantly studied experimentally. Has anything changed in this field in the most recent past?
2. Have you tried to compare the calculations for any of the studied systems with and without van der Waals corrections? What were the possible deviations?
3. Carboranedithiols on gold were used more as a test system. Are there any specific applications of these systems?
4. Have results obtained on similar systems been compared using DFT with a different basis set? For example for plane-wave basis set (VASP software)? What were the possible deviations?

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