February 12, 2024

Dear Editor and Reviewers,

We appreciate the thoughtful comments and questions regarding our manuscript (ID: materials-2830629) entitled " **Design and simulation of tunneling diodes with 2D insulators for rectenna switches**" by Evelyn Li, Prof. Zhao et al. submitted for publication in *Materials*. We have significantly benefited from your comments and improved our manuscript accordingly. The revised manuscript and our response to the reviewer's questions & comments are hereby submitted for your consideration. In addition, following the reviewers' suggestions, we have also modified the figures accordingly.

Please contact us if you have any further question.

Sincerely,

Evelyn Li
Prof. Erhai Zhao
Department of Physics and Astronomy
George Mason University
4400 University Drive, Fairfax, Virginia 22030
Phone: 703-993-4571
Email: ezhao2@gmu.edu

Reviewer 1:

Comments and Suggestions:

“The authors reported DFT calculations for 2D materials for selecting suitable tunnel barriers for tunneling diodes and the circuit simulations for the device characteristics of the tunneling diodes. The results point out a way to incorporate 2D materials, especially transition metal dichalcogenides, to design and fabricate tunneling diodes and related devices. This could contribute to the electronic industry. The work was well structured and the results presented are sound. The manuscript is also well-written and comprehensive. However, some points can be explained more clearly for the readers to understand better, and therefore, I suggest minor revision for this report before it can be published.”

Author Response: We are grateful to the reviewer’s nice words. We have revised the manuscript to address the reviewer’s concern. Our response to each question is shown in the following.

Questions and Responses:

Comment: “1. The authors use "oxidation and then relaxation" approach to carry out the DFT calculations for 2D Ti-based dichalcogenides. What is the advantage of this approach than "direct calculation" by putting the parameters into the supercells?”

Author Response:
This is a very good question. The “oxidation and then relaxation” approach in DFT simulation is to model the experimental process to obtain two-dimensional (2D) metal oxide insulators by oxidizing the 2D metal-sulfur layer materials. There are three major reasons for us to use this approach:
(1) In the nature, many 2D metal oxide insulators, such as Ti oxide, Sn oxide and Ta oxide layer materials, do not exist, although their bulk materials (in different atomic structures) can be commonly found. Therefore, it is unlikely (if not impossible) to find the correct natural parameters, such as bond lengths and angles of such 2D metal oxide insulators, to put into the

design of supercells for “direct calculation”. However, the 2D metal sulfur materials can be naturally found although most of them are semiconductors or semimetals.
(2) In our DFT simulation, the step of “oxidation followed with relaxation” is to model the mechanical relation after the sulfur atoms are replaced by oxygen atoms in the 2D materials. The relaxation process in simulation is to find out if a stable 2D metal oxide material can be obtained. In this work, the result indicated that the simulation was converged and a lowest and most stable energy state is reach for the proposed 2D metal oxide layer materials.
(3) Although previous experimental approaches were able to obtain some 2D metal oxides, such as TiO_2 layer materials by oxidizing TiS_2 layer materials, most of the detailed structural parameters of 2D metal oxide insulators are still unavailable.

Comment: “2. Why was the spin-orbit coupling (SOC) not considered in the DFT calculation? How does it relate to the underestimate of the band gap?”

Author Response:
We appreciate the reviewer’s valuable question. This will give us an opportunity to have a clear explanation.
spin-orbit coupling (SOC) is a relativistic interaction of an electron’s spin with its motion inside a potential sounding it. In general, SOC is included in the simulation of 2D materials when magnetic properties, Dirac Fermion of semimetals, spin hall effects and/or spin current are considered. According the reference [49] (added in the revised manuscript) “*Shi et al. Families of asymmetrically functionalized germanene films as promising quantum spin Hall insulators. Phys. Chem. Chem. Phys., 2021, 23, 3595-3605*” Table 1 and page 3596, quoted “the band gap opens up significantly when SOC is adopted in the simulation. The opening band gap arises from a downshifting of the VBM and an upshifting of CBM when compared to their counterparts without SOC”
Accordingly, the sentence in the manuscript (lines 201-206) is revised into

“The simulated band gap for monolayer materials can be wider if the spin-orbit coupling (SOC) and Heyd–Scuseria–Ernzerhof (HSE) functional are considered in calculation [47-50]. The SOC downshifts valence band maximum and upshifts conduction band minimum by including the

interaction of an electron's spin with its motion. [49] The HSE adds an additional potential by describing many-electron interactions and charge localization. [50]"

We have added two new references:

[49] Shi, L.; Li, Q. Families of asymmetrically functionalized germanene films as promising quantum spin Hall insulators. Phys. Chem. Chem. Phys. 2021, 23, 3595-3605.

[50] Flores, M.; Orellana, W.; Menendez-Proupin E. Accuracy of the Heyd-Scuseria-Ernzerhof hybrid functional to describe many-electron interactions and charge localization in semiconductors. Phys. Rev. B 2018, 98, 155131.

Comment: "3. For Figure 10(c), the output voltage versus AC frequency, it is a pity that no data points between 100 kHz and 800 THz. If there were, it would be more convincing. Moreover, what do the words "red" and "blue" represent? Why were the frequency 430 THz and 750 THz highlighted?"

Author Response:

We thank the reviewer for pointing out this confusing figure in our manuscript. The responses to the two comments are followed:

1. We did the PSpice simulation over a full range of frequencies from 10Hz to 1060Thz, with an exponential increase of frequency step and an emphasis on the fall-out frequencies from 800 THz. The frequencies between 1 THz and 800 THz were neglected in the simulation. In the revision, we did the circuit simulation on these frequencies, 1THz, 200 THz and 500 THz and replotted Figure 10(c). The simulation result showed a stable output at about 0.7 V.

2. The highlighted frequency range between 430 THz and 750 THz represents the visible light from red to blue light. We have revised the caption of Figure 10(c) to make it clear. In addition, we have revised the line 340-343 into:

"It should be noted that the output voltage is stable in the visible region from red (430 THz) to blue light (750 THz), very attractive for application in rectenna solar cells. Such a THz operation frequency range is also important for medical detection and high-speed telecommunication."