Dear Editor and Reviewers,

We sincerely thank you for taking the time to review our manuscript "Iron's impact on silicon solar cell execution: comprehensive modeling across diverse scenarios" (Ms. Ref. No.: MSB-S-24-02710). Your insightful comments and constructive suggestions have greatly helped us improve the quality of our work. We particularly appreciate your careful reading and thoughtful feedback, which have led to significant improvements in both the technical content and presentation clarity of our manuscript. We have carefully addressed all the comments and made corresponding revisions to the manuscript. Below we provide our detailed point-by-point responses to each comment. We hope the revised manuscript better meets your expectations and standards for publication in Materials Science and Engineering: B.

Response to Reviewer #1

Comment 1. *The author must explain the specific mechanisms you propose for the interaction between iron-related defects and other impurities in silicon solar cells? How might these interactions complicate the interpretation of photovoltaic performance metrics?*

Reply: In our study, we primarily focus on the impact of iron-related defects, particularly Fe_i and Fe_iB_s pairs, on the photovoltaic parameters of silicon solar cells. However, we acknowledge that the interaction of iron with other impurities (such as oxygen, carbon, or transition metals) can introduce additional complexities in interpreting photovoltaic performance.

Mechanisms of Interaction:

- **iron-oxygen complexes**: oxygen is a common impurity in Czochralski-grown silicon and can form stable complexes with interstitial iron (Fe_i-O). These complexes alter the recombination activity of Fe_i and may reduce the effectiveness of Fe_iB_s pair dissociation as a means to estimate iron concentration;
- **iron-carbon interactions**: carbon-related defects, such as Fe-C pairs, may modify the charge state of Fe_i, influencing its recombination properties and affecting the carrier lifetime. This interaction can lead to deviations in the expected trends of I_{SC} and V_{OC};
- **transition metal contamination**: if other transition metals (Cu, Ni, etc.) are present, they can introduce additional deep-level traps, competing with iron-related recombination centers. This may lead to non-monotonic behavior in efficiency trends, complicating the interpretation of photovoltaic responses.

Impact on Photovoltaic Metrics:

- the presence of multiple recombination centers can lead to overlapping effects in V_{OC} and I_{SC}, making it difficult to isolate the influence of Fe-related defects;
- some impurity interactions may cause non-monotonic trends in efficiency and fill factor changes, particularly under varying injection conditions;
- the temperature dependence of defect interactions may further introduce variability in photovoltaic responses, as different impurities have different activation energies.

Fe_iB_s pairs introduce deep-level recombination centers that strongly impact minority carrier lifetime, leading to reduced I_{SC} and V_{OC}. When Fe_iB_s pairs dissociate, the more mobile Fe_i leads to different recombination dynamics, which is particularly evident under monochromatic (940 nm) illumination. Our study demonstrates that changes in I_{SC} after Fe_iB_s dissociation can serve as a reliable method to estimate Fe concentration.

Comment 2. *The author should give the transient nature of defect dynamics, how do you assess the long-term stability of silicon solar cells in the presence of iron contamination? What experimental approaches would you recommend to study the aging effects of these defects over time?*

Reply:

The transient nature of defect dynamics, particularly the dissociation and recombination of Fe_iB_s pairs, plays a significant role in the long-term stability of silicon solar cells.

Long-term stability of silicon solar cells in the presence of iron contamination

Under illumination or thermal excitation, Fe_iB_s pairs dissociate into interstitial iron (Fe_i) and substitutional boron (B_s). In the absence of external excitation (e.g., during storage in the dark), Fe_i captures an electron and recombines with B_s, restoring the Fe_iB_s pair. This dynamic equilibrium between Fe_iB_s and Fe_i results in time-dependent variations in carrier lifetime and photovoltaic parameters. Over extended periods, Fe_i can diffuse and form precipitates, particularly at dislocations and grain boundaries. These precipitates act as deep recombination centers and may partially dissolve under elevated temperatures modifying solar cell performance.

Recommended experimental approaches to study aging effects:

- **time-Resolved Minority Carrier Lifetime Measurements:** quasi-Steady-State Photoconductance (QSSPC) and microwave photoconductance decay (μ-PCD) can track lifetime variations due to Fe_iB_s recombination-dissociation cycles. Measuring at different injection levels provides insight into the injection-dependent recombination activity of Fe_iB_s pairs;
- **deep-level transient spectroscopy (DLTS):** DLTS can resolve the capture cross-sections and activation energies of Fe-related defects, distinguishing Fe_i from Fe_iB_s states. This provides a quantitative approach to monitoring defect evolution over time;
- **illumination-induced defect metastability studies:** electroluminescence (EL) and photoluminescence (PL) imaging can spatially track Fe-related degradation over time;

Implications for silicon solar cell reliability:

- fluctuations in Fe_iB_s Pair Concentration impact solar cell efficiency due to time-dependent variations in recombination rates;
- iron precipitation vs. Fe_iB_s recombination equilibrium dictates whether degradation is reversible or permanent;
- understanding Fe_iB_s defect dynamics is critical for optimizing gettering strategies and passivation techniques to enhance long-term device performance;

Comment 3. *An Author should provide a theoretical framework for understanding how the temperature range you studied (290 K to 340 K) influences the activation energy of iron-related defects? How might this affect the performance of solar cells in varying environmental conditions?*
Reply:

The temperature range studied in our work (290 K to 340 K) was chosen to reflect realistic operating conditions of silicon solar cells, particularly those exposed to moderate climate variations. The behavior of iron-boron (Fe_iB_s) pairs and interstitial iron (Fe_i) is strongly temperature-dependent due to thermal excitation and defect migration effects. The key theoretical considerations include:

- Thermal dissociation of Fe_iB_s pairs:
  - the equilibrium between Fe_iB_s pairs and free Fe_i follows an Arrhenius-type relation, governed by the dissociation rate:

    $$k_\mathrm{d} = k_0 \exp(-\frac{E_\mathrm{a}}{k_\mathrm{b}T}), \tag{1}$$

    where k_d is the dissociation rate, E_a is the activation energy of Fe_iB_s dissociation, k_b is the Boltzmann constant, and T is the absolute temperature;
  - prior studies estimate Ea $\approx 0.7 - 0.8$ eV for Fe_iB_s dissociation in silicon;
  - as temperature increases, Fe_iB_s pairs dissociate more readily, increasing Fe_i concentration, which enhances recombination activity and reduces carrier lifetimes.
- Shockley-Read-Hall recombination dependence:

- the capture cross-section (σ) of Fe_i defects is temperature-dependent, influencing the recombination rate U given by:

$$U = \frac{\sigma v_{\mathrm{th}} N_{\mathrm{d}}}{1 + \exp(\frac{E_{\mathrm{t}} - E_{\mathrm{F}}}{k_{\mathrm{b}} T})}, \tag{2}$$

  where v_{th} is the thermal velocity of carriers, N_{d} is defect concentration, and E_{t} is the defect energy level;
- as temperature rises, carrier thermal velocity increases, altering the recombination dynamics and further impacting photovoltaic parameters.

The temperature-dependent behavior of iron-related defects has direct consequences on solar cell operation under different environmental conditions:

- Reduction in open-circuit voltage (V_{OC}):
  - increased FeB dissociation at high temperatures raises Fe_i concentration, enhancing Shockley-Read-Hall recombination. Since V_{OC} is governed by the equation:

$$V_{\mathrm{OC}} = \frac{k_{\mathrm{b}} T}{q} log \left(\frac{I_{\mathrm{SC}}}{I_0} + 1 \right), \tag{3}$$

    where I_0 is the saturation current, higher recombination rates increase I_0, leading to a reduction in V_{OC};
  - the observed temperature coefficient of ($V_{\mathrm{OC}} \approx -2.3 \frac{mV}{K}$) aligns with known iron-related degradation effects.
- Short-circuit current I_{SC} variability:
  - as Fe_i concentration rises, the minority carrier lifetime decreases, reducing carrier collection efficiency and thus I_{SC}. However, in certain temperature ranges, increased carrier mobility may partially compensate for these losses.
- Thermal cycling and long-term degradation risks:
  - field-deployed solar cells experience daily temperature fluctuations, which can lead to repeated FeB dissociation and recombination cycles, contributing to metastable defect states. Over time,Fe_i precipitation may lead to irreversible efficiency losses, especially in high-temperature climates.

Comment 4. *An Author mentioned the application of principal component analysis in evaluating impurity levels. Could you elaborate on how this technique was implemented in your study and its effectiveness in distinguishing between different types of impurities?*
Reply:

Comment 5. *Your paper discusses the influence of doping levels on the response of solar cells to iron contamination. Author should explain how varying the doping concentration affects the sensitivity of photovoltaic parameters to iron presence through the reference: Augmented photovoltaic performance of Cu/Ce-(Sn: Cd)/n-Si Schottky barrier diode utilizing dual-doped Ce-(Sn: Cd) thin films.*
Reply:

The primary reason doping concentration N_{B} influences the sensitivity of photovoltaic parameters to iron presence is that the N_{B} determines the Fermi level E_{F} position. In turn, the rate of Shockley-Read-Hall recombination — and consequently, variations in photovoltaic parameters due to iron impurities — depends on the relative positioning of E_{F} concerning the Fe_iB_s and Fe_i levels. Additionally, the equilibrium ratio of Fe_iB_s and Fe_i concentrations is also determined by the Fermi level position [1, 2]. Therefore, N_{B} affects the number of defects that change their state due to the complete dissociation of Fe_iB_s pairs, leading to corresponding relative changes in photovoltaic parameters analyzed in this study. Furthermore, according to Klaassen's model [3], the concentration of ionized impurities influences charge carrier mobility and, consequently, the diffusion coefficient D_n, diffusion length L_n, and photoelectric conversion efficiency (see Eqs. (4), (5), and (7) in the manuscript). However, the effect of N_B via D_n and L_n is significantly weaker than its influence through E_F variations. A minor effect is expected due to changes in free carrier absorption with varying doping levels. The impact of doping level on photovoltaic parameters has been studied in heterojunction [4], thin-film [5], and perovskite [6] solar cells. Moreover, it has been shown [5] that doping concentration variations affect other barrier structure parameters, such as saturation current and ideality factor.

This answer is incorporated in the text on page 4, paragraph 4, line 1-2. Reference is included in the revised manuscript (references 1)

> The recombination rate affects the value of L_n and, according to the Shockley–Read–Hall model, depends on trap concentrations, capture cross-sections of electrons and holes, temperature, the Fermi level E_F location, and defect levels. Temperature also affects the values of α and D_n. In turn, the position of E_F within the band gap depends on temperature and doping level. The relationship between N_B and E_F is the key factor in the influence of doping level on the sensitivity of photovoltaic parameters to iron presence. Specifically, the rate of Shockley-Read-Hall recombination — and consequently, variations in photovoltaic parameters due to iron impurities — depends on the relative positioning of E_F concerning the Fe_iB_s and Fe_i levels. Additionally, the equilibrium ratio of Fe_iB_s and Fe_i concentrations is also determined by the Fermi level position [50,51]. Therefore, N_B affects the number of defects that change their state due to the complete dissociation of Fe_iB_s pairs, leading to corresponding relative changes in photovoltaic parameters analyzed in this study. Furthermore, according to Klaassen's model [48], the concentration of ionized impurities influences charge carrier mobility and, consequently, the diffusion coefficient D_n, diffusion length L_n, and photoelectric conversion efficiency (see Eq. (4)). However, the effect of N_B via D_n and L_n is significantly weaker than its influence through E_F variations. A minor effect is expected due to changes in free carrier absorption with varying doping levels. The impact of doping level on photovoltaic parameters has been studied in heterojunction [59], thin-film [60], and perovskite [61] solar cells. Moreover, it has been shown [60] that doping concentration variations affect other barrier structure parameters, such as saturation current and ideality factor.

Comment 6. *In your findings, Author mentions that changes in short-circuit current under monochromatic illumination are the most reliable for estimating iron concentration. An author should provide more details on the methodology used to derive this conclusion and any potential limitations of this approach?*
Reply:

Comment 7. *An Author must improve the introduction section in the application part through the recent references CuO-La2O3 Composite-Enabled MIS Schottky Barrier Diodes: A Novel Approach to Optoelectronic Device Diversification; Enhancing photovoltaic applications through precipitating agents in ITO/CIS/CeO2/Al heterojunction solar cell; Manifestation on the choice of a suitable combination of MIS for proficient Schottky diodes for optoelectronics applications: A comprehensive review.*
Reply:

Response to Reviewer #2

Comment 1. *The abstract section should be more informative.*
Reply:
Comment 2. *The novelty of the work is missing in the introduction. Authors should explain what are the key advantages of iron's impact on silicon solar cell?*
Reply:
Comment 3. *Authors should improve the image quality of all figures.*
Reply:
Comment 4. *Author should explain how does the band alignment affect the overall performance of the solar cell?*

Reply:

Comment 5. *What are the primary sources of iron contamination in silicon used for solar cells?*

Reply:

Comment 6. *What role do recombination centers created by iron play in the modeling of solar cell performance?*

Reply:

Comment 7. *Author should discuss and cited recent Si based solar cell in the revised manuscript:* DOI : $10.1016/j.mseb.2024.117360$, DOI : $10.1016/j.mseb.2023.117141$, DOI : $10.1016/j.mseb.2024.117817$, DOI : $10.1007/s42247-024-00821-y$, DOI : $10.1016/j.inoche.2024.112785$

Reply:

Comment 8. *How does the modeling in this study contribute to the design of processes for impurity control in silicon?*

Reply:

Comment 9. *State the main findings in the conclusions.*

Reply:

References

[1] W. Wijaranakula, The reaction kinetics of iron–boron pair formation and dissociation in p–type silicon, J. Electrochem. Soc. 140 (1993) 275–281.

[2] J. D. Murphy, K. Bothe, M. Olmo, V. V. Voronkov, R. J. Falster, The effect of oxide precipitates on minority carrier lifetime in p–type silicon, J. Appl. Phys. 110 (2011) 053713.

[3] D. Klaassen, A unified mobility model for device simulation — I. model equations and concentration dependence, Solid-State Electron. 35 (1992) 953– 959.

[4] B. Sultana, M. Ferdous Rahman, A. Chandra Roy, M. Masum Mia, M. Al Ijajul Islam, A. Irfan, A. Rasool Chaudhry, M. Dulal Haque, A novel design and optimization of si based high performance double absorber heterojunction solar cell, Materials Science and Engineering: B 304 (2024) 117360.

[5] T. Akila, P. Gayathri, G. Alan Sibu, V. Balasubramani, H. Al-Lohedan, D. M. Al-Dhayan, Augmented photovoltaic performance of cu/ce-(sn:cd)/n-si schottky barrier diode utilizing dual-doped ce-(sn:cd) thin films, Opt. Mater. 149 (2024) 115133.

[6] M. Masum Mia, M. Faruk Hossain, M. Rahman, N. Badi, A. Irfan, M. Ferdous Rahman, Unveiling the impact of se based htm on bazrse3 perovskites solar cell and improving the theoretical efficiency above 32%, Materials Science and Engineering: B 311 (2025) 117817.