

Influence of point defects on laser-induced excitation in silicon

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We studied the influence of defect states on the laser excitation process in silicon using time-dependent density functional theory. We assumed two types of point defects: interstitial oxygen and silicon vacancies. We found that the photoabsorption efficiency increased with defect density in both cases owing to the color center. These defects distorted the crystal structure, thereby relaxing the selection rules and changing the indirect gap to direct. At low laser intensities, the defect states dominated the absorption process. However, as the laser intensity increased, the excitation efficiency approached that of crystalline silicon. In addition, we observed that the excitation efficiency did not scale linearly with the pulse length. Notably, in the case of Si vacancies, saturable absorption reduced photoabsorption significantly. Our results suggest that the existence of a defect induces the even-order high-harmonics generation. The enhancement of even-order high-harmonics generation by the silicon vacancy is larger than the interstitial oxygen.

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I. INTRODUCTION

In recent years, the use of intense laser pulses with durations ranging from femtoseconds to picoseconds has significantly advanced our understanding of laser-matter interactions. Ultrashort laser pulses are particularly important for the precise processing of gapped materials, as they allow nanostructuring without damaging the surrounding areas [1–6]. This precise control is essential for nanotechnology and materials science applications [7]. Laser processing encompasses a broad range of physics, including optics, quantum mechanics, material science, and thermodynamics, necessitating robust numerical modeling to comprehensively optimize and understand these processes. Over the years, the numerical modeling of laser excitation has progressed significantly [8–14], with silicon being a material of particular interest because of its fundamental scientific and industrial applications [15,16].

While theoretical studies have focused on single-shot processes with perfect crystals, the complexities of multipulse processing with various target qualities remain less explored. Multipulse processing introduces cumulative effects, such as temperature changes, structural modifications, and melting [17–19]. Recently, burst-mode processing has attracted interest because of its efficiency in exciting materials before thermal diffusion occurs [20]. During multishot irradiation, increased target temperatures can induce structural changes, including self-trapped excitons [21], surface morphology alterations, and fluid dynamics in molten materials [6]. Moreover, the quality of the target material, including doping, domain structures, defects, and composite structures, is crucial in laser processing. New computational methods that incorporate diverse material properties are required to accurately model laser processing in such complex materials. Owing to the complexity of nonperturbative effects, first-principles simulations are ideal for estimating laser excitation efficiency. Among these, time-dependent density functional theory (TDDFT) [22] is a highly accurate approach with a feasible computational cost, which has been applied successfully to nonperturbative laser excitation processes, contributing to our understanding of laser-induced damage [23–29]. To simulate laser-matter interactions, we have developed the scalable *ab initio* light-matter simulator for optics and

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nanoscience (SALMON) code, which is based on TDDFT [30].

In this study, we investigate the excitation of silicon in the presence of point defects. Point defects are crucial for both accumulation effects without noticeable structural changes and in the overall vulnerability of the material. The electronic structures of silicon with defects can be accurately calculated using first-principles approaches such as density functional theory (DFT) [31]. To fully understand the impact of defects on laser processing, their effects in nonlinear and nonperturbative regimes must be explored.

Our study used the SALMON code to focus on electron dynamics in silicon with typical point defects, specifically interstitial oxygen (O_i) and silicon vacancies ($Si-V$). This advanced simulation tool allowed us to model the complex interactions between intense laser fields and defect-laden silicon, providing insights into the underlying mechanisms of laser excitation and potential pathways for optimizing laser processing techniques.

The remainder of this paper is organized as follows. Section II describes the theoretical methods and numerical simulations. In Sec. III, the calculation results are presented and analyzed in detail. Finally, the conclusions are presented in Sec. IV.

II. COMPUTATIONAL METHOD

In the first step, we introduced point defects at arbitrary positions in a $4 \times 4 \times 4$ supercell containing 512 Si atoms. In the second step, we used DFT with QUANTUM ESPRESSO (QE) [32,33] to calculate the relaxed atomic structure, including the defects. Finally, the electron dynamics were calculated using SALMON.

For the atomic structure calculations, we used the pseudopotentials Si.pbesol-nl-rrkjus_psl.1.0.0.UPF and O.pbesol-n-rrkjus_PSL.1.0.0.UPF from the QE pseudopotential database (<http://www.quantum-espresso.org/pseudopotentials>), along with the PBEsol exchange-correlation potential [34]. The specific parameters used in the calculations are listed in Table I.

We employed the SALMON code for real-time electron dynamics calculations. The details of SALMON and its implementation can be found in [30]. The atomic structure calculated by QE was used to determine the ground state in the GS mode of SALMON by solving the Kohn-Sham

TABLE I. List of system and parameters for the QUANTUM ESPRESSO. Here “ n ” represents the number of defects in the cell.

System	Cell	N_k	Cutoff energy (Ry)
Si ₅₁₂ nO _i	$4 \times 4 \times 4$	2^3	80
Si _{512-n} nV _{Si}	$4 \times 4 \times 4$	2^3	120

TABLE II. List of parameters for SALMON.

System	N_k	N_r	Cell size (Å)
Si ₅₁₂ nO _i	Γ	88^3	$a = b = c = 21.72$
Si _{512-n} Si-nV	Γ	98^3	$a = b = c = 21.72$
c-Si	16^3	22^3	$a = b = c = 5.43$
a-Si (512 atom)	Γ	80^3	$a = b = c = 21.97$

equation:

$$\varepsilon_{b,\mathbf{k}} u_{b,\mathbf{k}}^G(\mathbf{r}) = \left[\frac{1}{2m} (-i\hbar\nabla + \hbar\mathbf{k})^2 - e\varphi^G(\mathbf{r}) + \hat{v}_{\text{NL}}^{\mathbf{k}} + v_{\text{xc}}^G(\mathbf{r}) \right] u_{b,\mathbf{k}}^G(\mathbf{r}). \quad (1)$$

Here, the scalar potential $\varphi(\mathbf{r}, t)$ includes the Hartree potential from the electrons and the local part of the ionic pseudopotentials, and $\hat{v}_{\text{NL}}^{\mathbf{k}} \equiv e^{-i\mathbf{k}\cdot\mathbf{r}} \hat{v}_{\text{NL}} e^{i\mathbf{k}\cdot\mathbf{r}}$. Here, $\hat{v}_{\text{NL}}$ and $v_{\text{xc}}(\mathbf{r}, t)$ are the nonlocal part of the ionic pseudopotentials [35] and the exchange-correlation potential, respectively. The parameters of SALMON are listed in Table II.

Although sophisticated exchange-correlation potentials, such as meta-GGA [36,37] provide better band gap estimates for silicon, their computational cost is nearly twice that of LDA potentials. Exciton absorption is important in the optical response of semiconductors. The change of exciton state due to defects, such as in the present study, is also considered to be important. In general, an accurate description of the exchange potential and/or two-electron dynamics is required to describe excitons. The hybrid functional theory such as HSE [38] and the nonequilibrium Green’s function method [39,40] are optimal for this purpose. However, there are many problems to be solved, such as the explosive increase in computational complexity for the hybrid functional and the increase in memory requirement for the nonequilibrium Green’s function method due to the need to store all wavefunctions of each time step. Therefore, we used LDA for $v_{\text{xc}}(\mathbf{r}, t)$ in this study [41].

The electron dynamics was calculated using the time-dependent Kohn-Sham (TDKS) equation:

$$i\hbar \frac{\partial}{\partial t} u_{b,\mathbf{k}}(\mathbf{r}, t) = \left[\frac{1}{2m} \left(-i\hbar\nabla + \hbar\mathbf{k} + \frac{e}{c} \mathbf{A}(t) \right)^2 - e\varphi(\mathbf{r}, t) + \hat{v}_{\text{NL}}^{\mathbf{k} + \frac{e}{\hbar c} \mathbf{A}(t)} + v_{\text{xc}}(\mathbf{r}, t) \right] u_{b,\mathbf{k}}(\mathbf{r}, t), \quad (2)$$

where $\mathbf{A}(t)$ is the applied vector potential. Solving the TDKS equation, we obtain the electric current in the unit-cell volume Ω as

$$\mathbf{J}(t) = \int_{\Omega} d^3r \mathbf{j}(\mathbf{r}, t) + \Delta \mathbf{J}_{\text{NL}}(t), \quad (3)$$

where $\mathbf{j}(\mathbf{r}, t)$ is the microscopic current density,

$$\mathbf{j}(\mathbf{r}, t) = -\frac{e}{m_e N_k} \text{Re} \sum_{\mathbf{k}, n} u_{n\mathbf{k}}^*(\mathbf{r}, t) \times \left\{ -i\hbar \nabla + \hbar \mathbf{k} + \frac{e}{c} \mathbf{A}(t) \right\} u_{n\mathbf{k}}(\mathbf{r}, t), \quad (4)$$

and $\Delta \mathbf{J}_{\text{NL}}(t)$ is a correction term stemming from the nonlocal potential:

$$\Delta \mathbf{J}_{\text{NL}}(t) = -e \int_{\Omega} d^3 r \frac{1}{N_k} \sum_{\mathbf{k}, n} u_{n\mathbf{k}}^*(\mathbf{r}, t) \times \frac{1}{i\hbar} \left[\mathbf{r}, \hat{v}_{\text{NL}}^{\mathbf{k} + \frac{e}{\hbar c} \mathbf{A}(t)} \right] u_{n\mathbf{k}}(\mathbf{r}, t). \quad (5)$$

The total energy of electrons in the unit cell is written as follows:

$$E_{\text{tot}}(t) = \int_{\Omega} d^3 r \frac{1}{N_k} \sum_{\mathbf{k}, n} u_{n\mathbf{k}}^*(\mathbf{r}, t) \hat{H}_{\mathbf{k}}^{\text{KS}}(t) u_{n\mathbf{k}}(\mathbf{r}, t) - \frac{e^2}{2} \int_{\Omega} d^3 r \int_{\Omega} d^3 r' \frac{n_e(\mathbf{r}, t) n_e(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} - \int_{\Omega} d^3 r V_{\text{xc}}(\mathbf{r}, t) n_e(\mathbf{r}, t) + E_{\text{xc}}[n_e](t), \quad (6)$$

where $E_{\text{xc}}[n_e](t)$ is the exchange-correlation energy functional, and $\hat{H}_{\mathbf{k}}^{\text{KS}}(t)$ is the time-dependent Hamiltonian in Eq. (2). The second and third terms compensate for the double counting of the Hartree and exchange-correlation potential terms, respectively, in the first term. According to the energy conservation, the excitation energy of electrons in the unit cell, $E_{\text{ex}}(t) \equiv E_{\text{tot}}(t) - E_{\text{tot}}(t=0)$, is equal to the absorbed energy $E_{\text{abs}}(t)$, or work done by the electric field, as follows:

$$E_{\text{ex}}(t) = E_{\text{abs}}(t) \equiv \int_0^t dt' \mathbf{J}(t') \cdot \mathbf{E}(t'). \quad (7)$$

The laser field is described by

$$\mathbf{A}(t) = \begin{cases} \mathbf{e}_z A_0 \cos^4\left(\frac{t}{T_p} \pi\right) \cos(\omega_0 t) & 0 < t < T_p, \\ 0 & T_p < t < T_e, \end{cases} \quad (8)$$

where A_0 and ω_0 denote the amplitude of the vector potential at the peak and the laser frequency, respectively. Here $\hbar\omega_0$ was set to 1.2 eV. The pulse length T_p was set to 40 fs and the computation was terminated at $T_e = 50$ fs.

III. RESULTS

A. Interstitial oxygen

Figure 1 compares the normalized density of states (DOS) for 1O_i and 8O_i with that of crystalline silicon ($c\text{-Si}$). The zero-energy level was set at the top of the occupied

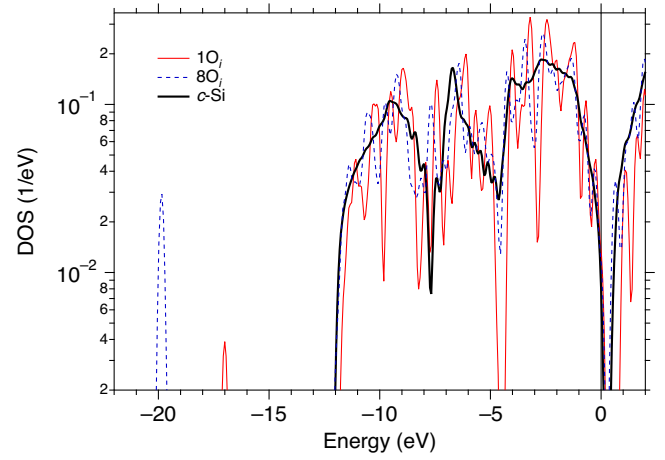


FIG. 1. Normalized density of states of 1O_i (red solid line), 8O_i (blue dashed line), and $c\text{-Si}$ (black thick line).

energy state. Despite the overall similarity of the DOS structures, a peak associated with oxygen occurs at approximately -20 eV. Oxygen atoms attract electrons from silicon, creating deeply bound states around the defects, which do not significantly contribute to the laser excitation.

Figure 2 shows the dielectric function $\varepsilon(\omega)$. The calculated optical bandgap (E_o) is approximately 2.5 eV, which is smaller than the experimental value (3.1 eV) owing to the use of the LDA potential. Variations in $\varepsilon(\omega)$ below E_o are significantly dependent on the oxygen density. While

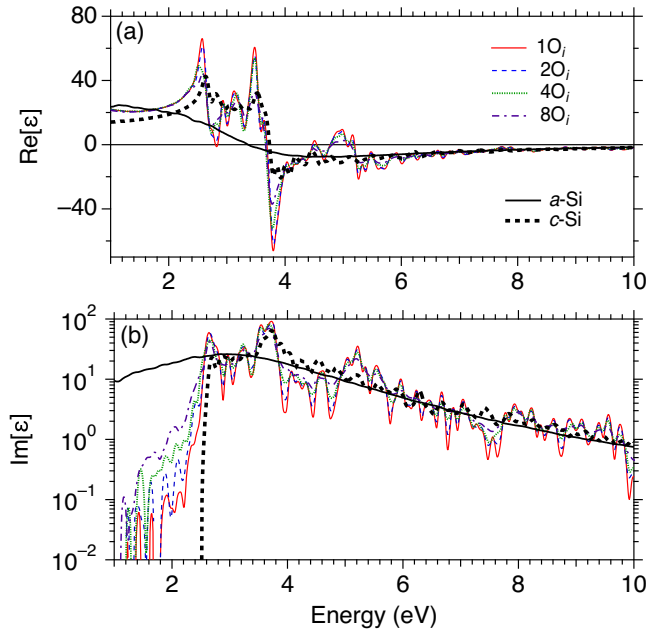


FIG. 2. Dielectric function corresponding to various interstitial oxygen densities. $c\text{-Si}$ and $a\text{-Si}$ are shown as references for the extreme cases.

the real part of $\varepsilon(\omega)$ [Fig. 2(a)] exhibits minimal dependence on defect density, several peaks in the imaginary part [Fig. 2(b)] indicate the presence of color center states below E_o . Below E_o , absorption increases with the oxygen density, approaching the spectrum of amorphous Si (*a*-Si). This trend suggests a blue shift in the optical bandgap due to the distortion of the crystal structure around the defects, which disrupts the symmetry of the system.

Figure 3 shows the time evolution of (a) current, (b) energy absorption under various intensities, and (c) energy absorption of different O_i densities. The pulse length T_p was set to 40 fs, and the computations were terminated at $T_e = 50$ fs. The laser intensity was scaled to the intensity (I) of the incident pulse by using the following relationship:

$$I = \left(\frac{1 + n_{\text{Si}}}{2} \right)^2 I_m. \quad (9)$$

Here, I_m is the laser intensity experienced by the electrons and $n_{\text{Si}} = \sqrt{20}$ is the refractive index calculated from the real part of $\varepsilon(\omega = 1.2 \text{ eV})$, which remains almost unaffected by defects [Fig. 2(a)]. The dashed lines indicate the dependence of the one- and two-photon processes. The electric field and current shown in Fig. 3(a) are the results of a very strong case that exceeds the processing threshold.

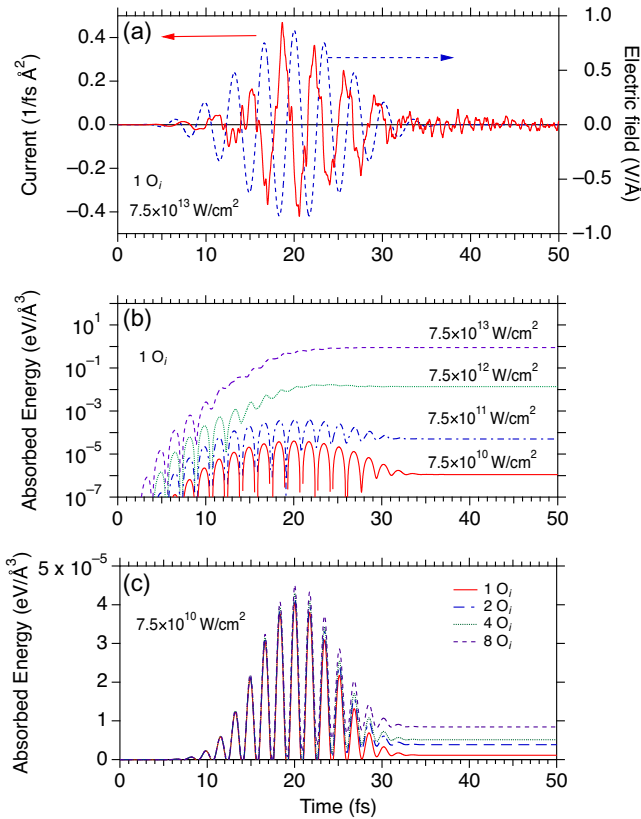


FIG. 3. Electron dynamics and energy absorption with O_i .

The incident laser intensity is $7.5 \times 10^{13} \text{ W/cm}^2$, and the system contains only one oxygen atom. The current has fine oscillations from the beginning of the pulse and continues to oscillate even after the pulse has passed. This is a typical response when strong electronic excitation occurs. Figure 3(b) shows how the energy absorbed by the electrons increases with laser intensity. At the lower laser intensity of $7.5 \times 10^{10} \text{ W/cm}^2$, oscillation of energy consistent with the electric field period is seen. This is the dielectric response seen at photon energies lower than the optical gap. As the laser intensity increases, these oscillations become less visible, indicating that efficient photon absorption is occurring. As discussed in the following, the effect of defects is more pronounced with weak lasers. Therefore, the dependence on oxygen defect concentration at low laser intensity is shown in Fig. 3(c). The energy absorption increases as the concentration increases.

Figure 4(a) illustrates the dependence of the absorbed energy density on the laser intensity at various oxygen densities. The black solid line with diamonds represents the case of crystalline silicon (*c*-Si). At low intensities, the one-photon process dominated in the presence of O_i . In contrast, *c*-Si exhibits a three-photon process at approximately $1 \times 10^{12} \text{ W/cm}^2$. Above $1 \times 10^{13} \text{ W/cm}^2$, all cases exhibit similar excitation energies. The electron temperature dependence was examined up to 1000 K;

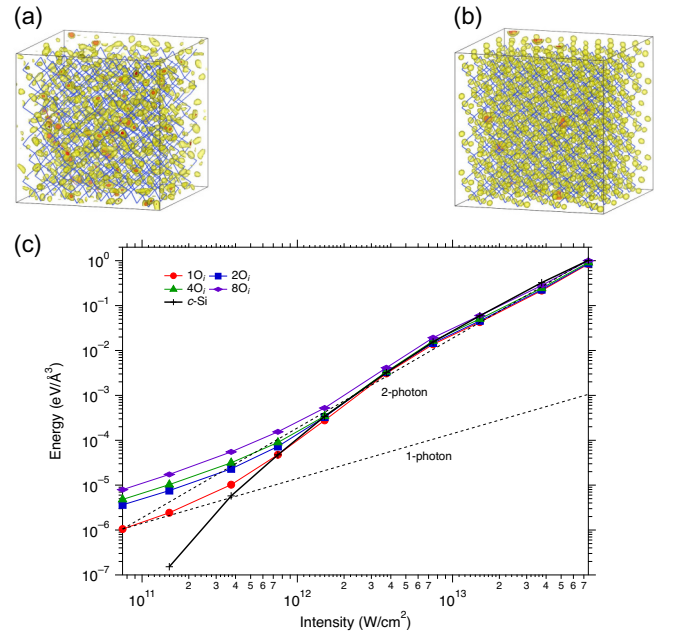


FIG. 4. (a) Absorbed energy density as a function of the peak laser intensity. The laser intensity is scaled to the incident intensity using $\text{Re}[\varepsilon(\omega = 1.2 \text{ eV})] = 20$ in Fig. 2. (b),(c) Change in the electron density ($\Delta\rho$) from the ground state. The red and yellow isosurfaces indicate $\Delta\rho = -6.8 \times 10^{-4} \text{ \AA}^{-3}$ and $\Delta\rho = -3.4 \times 10^{-4} \text{ \AA}^{-3}$, respectively.

however, no significant temperature dependence was observed.

To gain detailed insight into the excitation process, contour plots of the electron density for $8O_i$ are also shown. The change in electron density ($\Delta\rho$) indicates electron excitation. The red and yellow isosurfaces, which were drawn using VESTA [42], represent $\Delta\rho = -6.8 \times 10^{-4} \text{ \AA}^{-3}$ and $\Delta\rho = -3.4 \times 10^{-4} \text{ \AA}^{-3}$, respectively. Nonuniform excitation occurs at the lowest intensity (Fig. 4(b)). This observation, along with the relatively continuous absorption shown in Fig. 2(b), suggests that the breaking of crystal symmetry due to defects plays a significant role. The excitation becomes more uniform (Fig. 4(c)) as the laser intensity increases. This transition from nonuniform to uniform excitation indicates a shift from a one-photon process associated with defects to a nonlinear process in bulk Si. The Keldysh parameter reached unity at a laser intensity of $7 \times 10^{14} \text{ W/cm}^2$, which is beyond the range of our calculations. Therefore, the transition from local to uniform excitation can be attributed to higher-order photoabsorption processes, rather than tunneling.

B. Silicon vacancy

Si- V is a common defect. Although they may exist before laser irradiation they could also be created by the high temperature of silicon after irradiation. Figure 5 shows the normalized DOS for Si-1 V , Si-8 V , and c -Si. The energy is defined as the energy of the highest occupied energy state. Some peaks are observed around 0 eV, which do not exist in O_i . These peaks imply intense color-centered absorption.

Figure 6 illustrates the dielectric function of Si with respect to Si- V . Although the real part of ϵ does not change significantly, the change in $\text{Im}[\epsilon]$ owing to the color centers

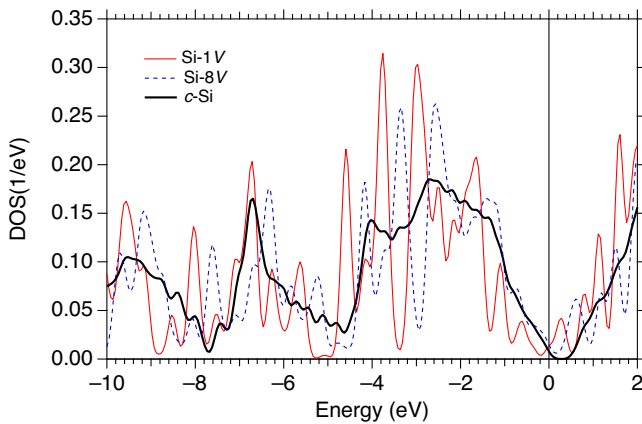


FIG. 5. Density of states with silicon vacancies. Here 0 eV is defined by the highest occupied state.

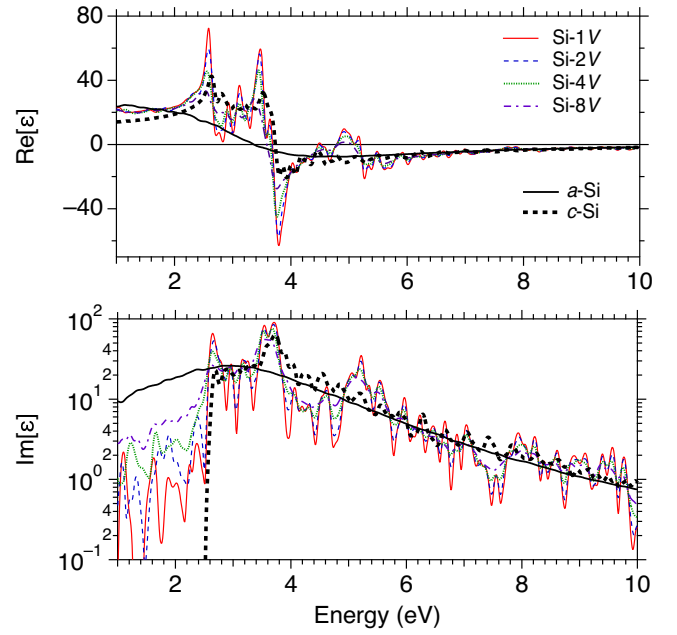


FIG. 6. Dielectric functions with silicon vacancies.

is more intense than that caused by the O_i . Si- V creates dangling bonds and distorts the crystal structure via Jahn–Teller distortion [43,44]. Therefore, as the density of Si- V increases, the optical gap exhibits a larger blue shift and intense absorption by the color centers. The blue shift is also larger than that due to O_i .

Figure 7(a) shows the dependence of the electron excitation on the laser intensity and Si- V density. The one-photon process dominates in all cases below an intensity of $1 \times 10^{13} \text{ W/cm}^2$. The energy density does not correlate with the defect density in this regime. Because $\text{Im}[\epsilon]$ in Fig. 6(b) indicates nearly the same one-photon absorption intensity at 1.2 eV, Si-1 V and Si-2 V have similar absorbed energies. This result highlights the importance of defect states in laser excitation.

Also illustrated are $\Delta\rho$ for Si-8 V at $7.5 \times 10^{11} \text{ W/cm}^2$ (Fig. 7(b), with surfaces of $\pm 0.002 \text{ \AA}^{-3}$) and $7.5 \times 10^{13} \text{ W/cm}^2$ (Fig. 7(c), with surfaces of $\pm 0.047 \text{ \AA}^{-3}$). The yellow and cyan surfaces represent positive and negative $\Delta\rho$, respectively. At low intensities, excitation occurs in relatively localized areas compared with the O_i case, suggesting strong absorption by the color centers. At higher intensities, the excitation becomes more uniform, similar to the O_i case, and the excitation energies approach those of c -Si. This indicates that color centers and defect states significantly affect excitation at lower intensities, whereas bulk silicon properties dominate at higher intensities. The linear response calculations (Figs. 2 and 6) show that $\text{Im}[\epsilon]$ remains unchanged above E_o , which is consistent with the behavior in the high-intensity regime (Figs. 4 and 7). Multiphoton absorption above the optical bandgap is unaffected by defects.

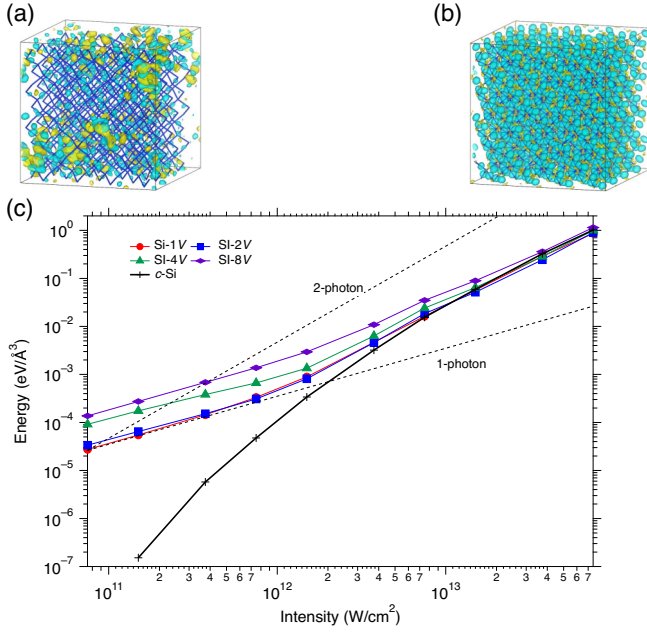


FIG. 7. (a) Intensity dependence of the absorbed energy density with Si- V . (b),(c) Change of the electron density from the ground state. The cyan and yellow isosurfaces indicate $\Delta\rho = -0.002 \text{ \AA}^{-3}$ and $\Delta\rho = 0.002 \text{ \AA}^{-3}$, respectively.

C. Defect type dependence

In this subsection, we explore the dependence of optical properties on defect types in Si, focusing on how color centers and their associated defects influence photoabsorption efficiency and nonlinear optical responses.

Defect types, particularly color centers, are critical in determining the optical characteristics of materials. Although these color centers can enhance photoabsorption efficiency significantly, their effectiveness is inherently constrained by their density. When the excitation at a color center reaches saturation, a phenomenon known as saturable absorption occurs, which limits the overall efficiency of the material.

Figure 8 illustrates the pulse-duration dependence of the interstitial oxygen [O_i ; Fig. 8(a)] and silicon vacancies [Si- V ; Fig. 8(b)]. When photoabsorption is unsaturated, the absorbed energy typically increases linearly with pulse duration. However, for O_i , this relationship is not strictly linear, although the dependence on the laser intensity remains similar. This suggests a weak saturation of photoabsorption in O_i and indicates that while saturation effects are present, they do not dominate the behavior. In contrast, the pulse duration dependence of Si- V exhibits characteristics that differ from those of O_i . Specifically, the excitation energies of the $T_p = 80$ fs and 120 fs pulses remain nearly identical at approximately an intensity of $1 \times 10^{12} \text{ W/cm}^2$. This behavior indicates saturable absorption in silicon vacancies at this intensity level. The differences arise from the underlying absorption

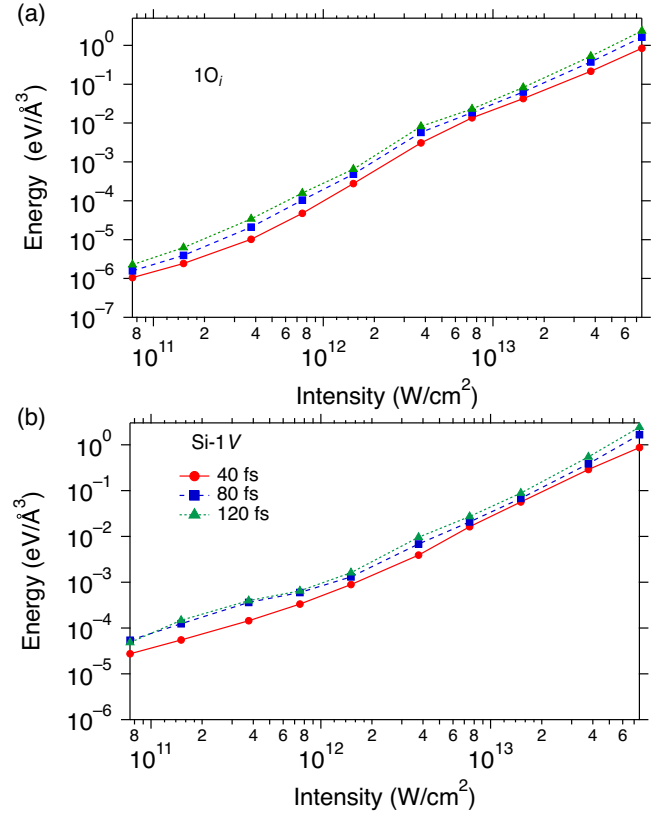


FIG. 8. Pulse duration dependence of (a) $1O_i$ and (b) Si-1 V .

mechanisms: while interstitial oxygen ($1O_i$) involves relatively weak one-photon absorption necessitating higher-order photon processes, the one-photon absorption process is dominant in silicon vacancies (Si-1 V), leading to a pronounced saturable absorption effect in Si-1 V .

Next, we discuss how defects influence the nonlinear optical response, particularly in high-harmonic generation (HHG). HHG reflects the symmetry of the system. In c -Si, which possesses inversion symmetry, only odd-order harmonics are allowed. However, when defects break this symmetry, even-order harmonics and differential frequency generation (DFG) are possible. Figure 9 presents the HHG spectrum under a laser intensity of $7.5 \times 10^{10} \text{ W/cm}^2$ as a function of harmonic order. The vertical axis represents the intensity of the Fourier-transformed electronic current. For both defect types, the intensities of the even-order harmonics and DFG increase as a function of the defect density. The Si vacancies shown in Fig. 9(b) demonstrate a significant increase in DFG and second-harmonic generation compared with interstitial oxygens, as shown in Fig. 9(a). This result implies that the distortion of the crystal structure by silicon vacancy is larger than that by the interstitial oxygen. It is noteworthy that the $1O_i$ defect configuration exhibited more intense even-harmonic generation than the $2O_i$ configuration did. This

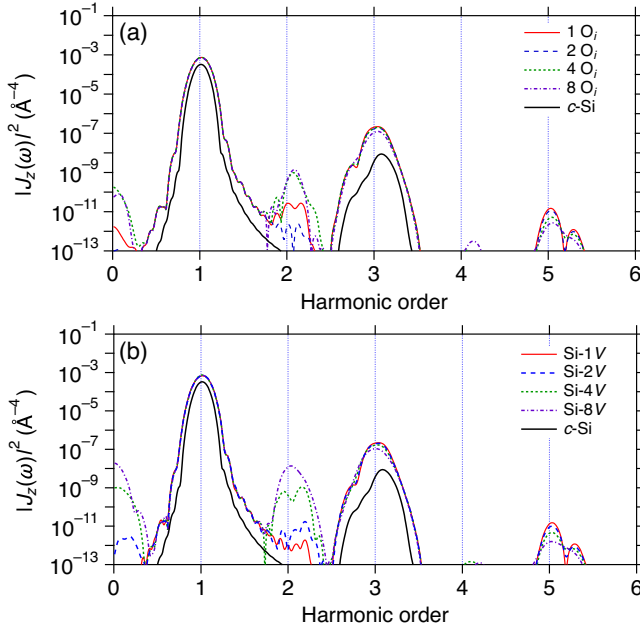


FIG. 9. High-harmonic generation with (a) interstitial oxygens and (b) silicon vacancies. The incident laser intensity is assumed to be 7.5×10^{10} W/cm².

result underscores the importance of defect positioning in determining how defects disrupt the symmetry of *c*-Si.

Figure 10 shows the intensity dependence of (a) 8O_i and (b) Si-8V, which have strong even-order HHG in

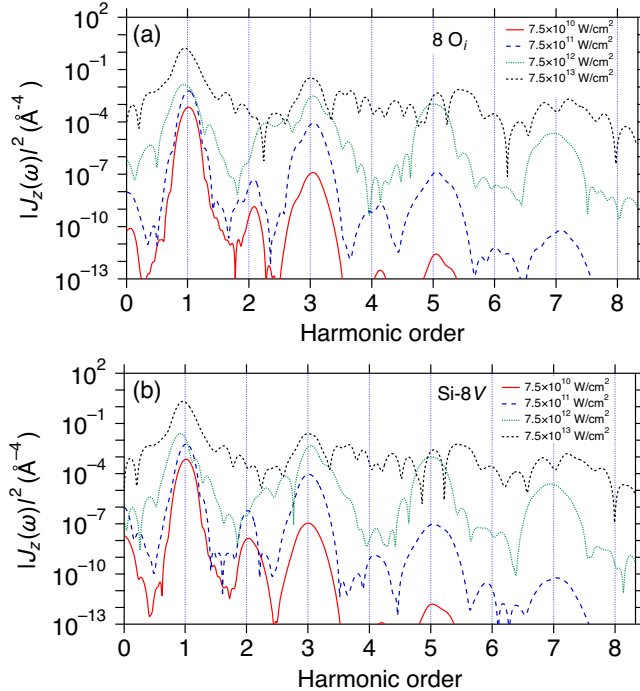


FIG. 10. Laser intensity dependence of high-harmonic generation with (a) interstitial oxygens and (b) silicon vacancies.

Fig. 9. For both defect types, even harmonics and DFG can be seen up to 7.5×10^{11} W/cm², but the signals become indistinguishable above 7.5×10^{12} W/cm². In particular, at 7.5×10^{13} W/cm², the spectra of interstitial oxygen and silicon defects are almost identical. This intensity dependence is consistent with the results that the bulk silicon response becomes dominant from the intensity above 1×10^{13} W/cm². Up to about 1×10^{13} W/cm², the defect-derived response is relatively strong, and even-order HHGs due to symmetry breaking can be seen. Above that level, however, interband transitions similar to those in *c*-Si become dominant, and the odd-order HHG becomes dominant.

IV. SUMMARY

In this study, we have used TDDFT to investigate the laser excitation process of silicon with defect states. Interstitial oxygen atoms and silicon vacancies were considered examples of point defects. Our findings revealed significant enhancement in photoabsorption owing to the defect states at low-intensity region. However, at higher intensities, the excitation energy was nearly identical to that of defect-free Si. Thus, at higher intensities, the excitation from the valence band to the conduction band of bulk Si via higher-order photon processes dominated, rendering the influence of the defects negligible. In addition, we have observed that the enhancement effect of the defect states was constrained by the pulse length because saturable absorption occurred with relatively weak and long laser pulses. Furthermore, we suggest that distortion of the symmetry by defects induces the even-order-harmonic generation and DFG.

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