

Hole trapping facilitates the formation of Frenkel pairs in crystalline and amorphous Ga₂O₃ films

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Holes are injected from electrodes or produced by irradiation in many applications of crystalline and amorphous Ga₂O₃. They are known to trap in polaron states in both phases. We investigate, using density functional theory, how hole trapping in Ga₂O₃ can lead to creation of Frenkel pairs (FPs) of oxygen vacancies in the +2 charge state, V_O²⁺, and interstitial oxygen atoms. The calculations reveal that hole bipolarons lead to the formation of O–O dimers, distorting adjacent Ga–O bonds and resulting in a significant reduction of the barriers for the nearest-neighbor FP formation with respect to pristine structures. In amorphous Ga₂O₃ the barriers are on average 2.05 eV, much lower than in the crystalline phase, where they are 3.47 to 4.80 eV. Furthermore, in the amorphous phase, the migration barriers for oxygen vacancies in the +2 charge state, V_O²⁺, are reduced compared to those in the crystalline phase, indicating that V_O²⁺ can drift away under the influence of electric fields, creating stable defects. These results show that hole trapping in Ga₂O₃ can facilitate the formation of FPs, particularly in amorphous structures. They can be useful in understanding the mechanisms of degradation in Ga₂O₃ based devices under negative bias and illumination stress.

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I. INTRODUCTION

Crystalline β -Ga₂O₃ and amorphous (a) Ga₂O₃ are used in many applications both as a channel and as a dielectric layer due to the large band gap (approximately 5.0 eV) and high electron mobility [1–3]. These applications include metal-oxide-semiconductor field-effect transistors (MOSFETs) [4,5], power diodes [6–10], solar blind photodetectors [11–13], memristor devices [14–16], x-ray detectors [17–19], and pressure sensors [20,21]. In these devices, electrons and holes are either injected into Ga₂O₃ films from electrodes or created by photons or other types of irradiation.

The results of previous research show that β -Ga₂O₃ has high electron mobility and no intrinsic electron trapping [22–26], but can trap holes, resulting in the formation of small polarons [26–29], which have been confirmed experimentally and theoretically. In addition to reduced hole mobility, hole trapping can pose challenges for the long-term stability of Ga₂O₃-based devices, such as charging and degradation. Experimental studies [30–32] and theoretical calculations in other oxides, such as HfO₂, have demonstrated the detrimental role of hole trapping and the ability of trapped holes to form bipolarons and reduce barriers for the creation of Frenkel pairs [33]. Binding of localized holes and formation of bipolarons

has been suggested in several other metal oxides, such as Al₂O₃, anatase TiO₂, V₂O, MoO₃, and InGaZnO (see discussion in Refs. [34–37]).

We have recently studied the possibility of formation of hole bipolarons in crystalline and amorphous Ga₂O₃ [29] and found that they are stable with respect to separated holes, with a wide range of binding energies, averaging at 0.2 eV. In the amorphous phase, the binding energy is distributed due to variations in local environment and can exceed 0.5 eV, indicating stability of bipolarons at room temperature.

β -Ga₂O₃-based devices are susceptible to degradation under specific operational stresses, such as negative bias stress (NBS) applied to achieve an off state [38,39]. NBS can cause the injection of holes into the oxide layer if appropriate states are available. The instability of amorphous Ga₂O₃ thin-film transistors under stress conditions has also been demonstrated, particularly after exposure to NBS [40] and irradiation by x rays [18,41]. These observations indicate that both crystalline and amorphous Ga₂O₃ films can be susceptible to defect formation due to NBS or photon exposure, both of which produce holes in a sample. However, the detailed mechanisms for defect formation in Ga₂O₃ remain unclear.

Previous research of other wide-band-gap oxides, such as SiO₂, HfO₂, and Al₂O₃, used as dielectrics in MOSFETs, has shown that barriers for the formation of FPs of oxygen vacancies and interstitial oxygen atoms are strongly reduced when electrons or holes injected from electrodes are trapped in the oxide in localized bipolaron states [33,42–46]. In particular, in amorphous HfO₂, the formation of electron and hole bipolarons can result in the formation of FPs [33] contributing to the dielectric breakdown of gate oxide films [45]. In contrast, in Ga₂O₃ only hole trapping occurs [26,27,29]. Therefore, in

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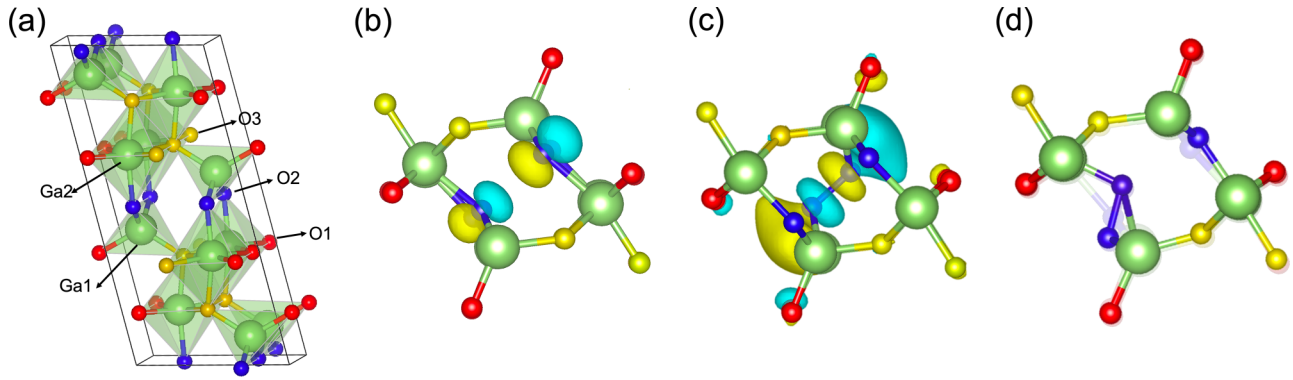


FIG. 1. Structure of β -Ga₂O₃. (a) Conventional cell. (b) Two-center self-trapping of a hole (STH). (c) Hole bipolaron. (d) Oxygen split-interstitial configuration in 0 charge state (O_{si}^0). Green spheres represent Ga atoms, while red, blue, and yellow spheres indicate O1, O2, and O3 atoms, respectively.

this work, we investigate the mechanisms and barriers of FP creation caused by hole trapping and the formation of hole bipolarons in Ga₂O₃ using density functional theory (DFT) simulations with the PBEsol functional.

The results show that, similar to other oxides, the bipolaron formation strains adjacent Ga-O bonds and strongly reduces barriers to FP formation. These barriers are much lower in the amorphous phase, where they average 2.05 eV, compared to 3.47 to 4.80 eV in the crystalline phase. In addition, vacancy migration barriers are lower in the amorphous structure, which facilitates the separation of nascent FPs into more stable defects. These results suggest a plausible mechanism of how hole injection (e.g., under irradiation and high voltage negative bias stress), particularly in Ga₂O₃ x ray and photodetectors, can lead to the creation of oxygen vacancies and interstitial atoms, which can affect device performance.

II. METHODOLOGY

All DFT calculations were performed using the Gaussian plane wave (GPW) method [47] as implemented in the CP2K software package [48]. The calculations were carried out for both pristine supercells and defective structures at the Γ point, with a plane-wave cutoff energy of 600 Ry, using a supercell of 400 atoms as done in previous work [29]. We used the DZVP-MOLOPT-SR-GTH-q13 Gaussian basis set for Ga and DZVP-MOLOPT-SR-GTH-q6 for O [49] with the Goedecker-Teter-Hutter (GTH) pseudopotentials [50]. Most calculations were performed using the PBEsol functional [51]. We used the crystalline and amorphous structures produced and described in previous work [29].

The β -Ga₂O₃ structure is characterized by two types of Ga atoms in tetrahedral and octahedral coordinations of O atoms, of which there are three unique types, as shown in Fig. 1(a). The results of previous work [26,27,29] have shown that holes can become self-trapped at all three types of oxygen sites, (O1, O2, and O3) in β -Ga₂O₃. In particular, the self-trapped hole (STH) on the O2 site, which is surrounded by two tetrahedral Ga (Ga1) atoms and one octahedral Ga (Ga2) atom in the crystalline β phase, forms a two-center trapping configuration shared between two O2 atoms [see Fig. 1(b)]. Subsequent injection of a second hole into this configuration enables the formation of a peroxide (O-O bond) with a

binding energy of approximately 0.2 eV [29], also referred to as a hole bipolaron shown in Fig. 1(c). Although a hole bipolaron can be formed at any O2 sites, it is unstable when the second hole is injected into the STH at O1 (surrounded by one Ga1 and two Ga2 atoms) or O3 (surrounded by one Ga1 and three Ga2 atoms).

As discussed in [29], the top of the valence band in the amorphous phase is dominated by several strongly localized states, which correspond to two-coordinated O ions with a wide Ga-O-Ga angle or to sites with two O ions located closer than 2.8 Å to each other. We call these sites “precursors” because holes introduced into a periodic cell spontaneously localize at these O sites. We observed the one-center and two-center hole localization in different structures, which can be characterized by four configurations [29]: (a) single-O (CN = 2), (b) paired-O (CN = 2), (c) paired-O (CN = 2 and 3), and (d) paired-O (CN = 3 and 3). We did not observe hole trapping on four-coordinated or single three-coordinated O atoms. The two-center hole configurations have larger trapping energies. There is a lowest-energy hole bipolaron configuration in each amorphous cell. These configurations were recalculated in this work using the functional PBEsol [51], which can successfully reproduce the formation of hole bipolarons and the corresponding structures.

We aim to model the reaction $\text{Ga}_2\text{O}_3 + 2h^+$ (hole bipolaron) $\rightarrow V_O^{2+} + O_{si}^0$ (FP), where V_O^{2+} is an oxygen vacancy in the +2 charge state and O_{si}^0 is the split interstitial in the 0 charge state. However, it is computationally difficult to find the stable FP structure by simply displacing an O ion from the bipolaron site. First, possible stable FP configurations in the vicinity of a bipolaron need to be identified. To achieve this, in the β phase, the split-interstitial O_{si}^0 configuration on the O2 site [see Fig. 1(d)] investigated in previous work [52] was used. The interstitial oxygen defect in the 0 charge state has been shown to form as O_{si}^0 with an O-O dimer around 1.4 Å [52,53]. Then, nearby O ions were removed to create different nearest-neighbor (NN) FP structures $V_O^{2+} + O_{si}^0$ with three different positions of V_O^{2+} with respect to O_{si}^0 .

The same procedure for preparing the FPs was used in the amorphous phase. Out of the distribution of hole bipolarons obtained in 20 amorphous structures in Ref. [29], we have chosen four configurations which have medium and

TABLE I. Reactions of FPs formation in β -Ga₂O₃, relative energy (E_{rel}) with respect to the initial state, forward barriers (E_b^f), recombination barriers (E_b^r) in eV, and atomic displacements for O–O dimer (D1) and to form V_O (D2), both in Å, using CI-NEB with PBEsol.

Initial state	Final state	E_{rel}	E_b^f	E_b^r	D1	D2
β -Ga ₂ O ₃ + 2h ⁺ (hole bipolaron)	$V_{O1}^{2+} + O_{si}^0$	2.33	3.47	1.14	1.58	2.61
	$V_{O2}^{2+} + O_{si}^0$	3.05	4.80	1.75	1.59	3.00
	$V_{O3}^{2+} + O_{si}^0$	1.55	3.96	2.41	1.81	3.23
β -Ga ₂ O ₃ (no bipolaron)	$V_{O1}^0 + O_{si}^0$	7.47	7.75	0.28	3.04	2.73
	$V_{O2}^0 + O_{si}^0$	6.57	7.06	0.49	3.03	2.91
	$V_{O3}^0 + O_{si}^0$	7.31	7.50	0.19	3.03	2.37

high bipolaron binding energies of 0.3–0.7 eV, such that they can remain stable at room temperature. However, in the amorphous phase, there are no distinct oxygen lattice sites. Therefore, two different O atoms were removed for each of the four different amorphous samples to create FPs. The resulting eight FP configurations provide a consistent qualitative model of the effect of hole trapping on defect creation.

The energy barriers for the creation of FP were then calculated for the reaction: Ga₂O₃ + 2h⁺ (hole bipolaron) → $V_O^{2+} + O_{si}^0$ (FP), using the CI-NEB method [54] implemented in CP2K [55]. Each defect formation path was simulated using seven images. In the crystalline β phase, we have reevaluated reactions using the transition state dimer method (TS-DM) [56] with the PBE0-TC-LRC hybrid functional [57], using a Hartree-Fock exchange truncation radius of 5 Å and 30% Hartree-Fock exact exchange from the previous work [29]. This functional provides band gaps of around 5.05 eV and 4.3 eV for the β and amorphous phases, respectively. This is detailed in the results section. To study the stability of the NN FP structures, migration of V_O^{2+} was examined using the CI-NEB method.

III. RESULTS OF CALCULATIONS

A. Formation of Frenkel pairs in β -Ga₂O₃

The formation of a hole bipolaron causes a significant structural distortion of the pristine structure. It elongates the Ga–O bonds from their pristine bond lengths by increasing the Ga1–O2 distance from 1.84 Å to 2.08 Å and the Ga2–O2

distance from 1.94 Å to 2.28 Å [29]. This lattice distortion and deformation of nearby Ga–O bonds can facilitate the formation of FPs, which comprise a V_O^{2+} and O_{si}^0 .

To explore this reaction, the FP structures were modeled considering an oxygen split-interstitial configuration O_{si}^0 as seen in Fig. 1(d) and three different V_O sites, as described in Table I. The reaction: Ga₂O₃ + 2h⁺ → $V_O^{2+} + O_{si}^0$ (FP) is illustrated schematically in Fig. 2. The initial configuration in Fig. 2(a) corresponds to a hole bipolaron that creates a peroxide O–O bond and is equivalent to that shown in Fig. 1(c). Subsequently, in the transition state Fig. 2(b), this O–O dimer is displaced into a split interstitial configuration (displacement 1). This is accompanied by a significant lattice distortion, where the displacement of nearby oxygen ions restores a Ga–O bond and results in the formation of an oxygen vacancy in the +2 charge state (displacement 2). The values of these two largest atomic displacements of O are listed as D1 (O–O dimer displacement) and D2 (V_O formation) in Table I.

The final configuration, shown in Fig. 2(c), represents a stable NN FP. Three stable final FP structures $V_O^{2+} + O_{si}^0$ are shown in Figs. 3(a)–3(c). The corresponding energy barriers (E_b^f) are 3.47 eV, 4.80 eV, and 3.96 eV for the sites V_{O1}^{2+} , V_{O2}^{2+} , and V_{O3}^{2+} , respectively, with the relative energy profiles shown in the Supplemental Material Fig. S1(a) [58]. These barriers were reevaluated using the TS-DM method [56] with the PBE0-TC-LRC hybrid functional [57] used in the previous work [29]. Starting from the saddle point obtained via CI-NEB calculations using the PBEsol functional, the E_b^f for FP formation was calculated to be 3.53 eV, 5.13 eV, and 4.04 eV for FP: $V_{O1}^{2+} + O_{si}^0$, $V_{O2}^{2+} + O_{si}^0$, and $V_{O3}^{2+} + O_{si}^0$, respectively (see Table S1 [58]). These values are slightly higher than the results obtained using the CI-NEB approach.

In contrast, when starting from a pristine structure without a hole bipolaron, the energy barriers to form FP, $V_O^0 + O_{si}^0$, are significantly higher, with values of 7.75 eV, 7.06 eV, and 7.50 eV for the V_{O1}^0 , V_{O2}^0 , and V_{O3}^0 sites, respectively. The relative energy profiles for these reactions are shown in Fig. S1(b). FP structures of $V_O^0 + O_{si}^0$ in different V_O sites are shown in Figs. 3(d)–3(f).

We have also checked the energies of FP structures in the $V_O^{1+} + O_{si}^{1+}$ charge configuration. These were produced by optimizing the geometry of the triplet state of the $V_O^{2+} + O_{si}^0$ configuration. As one can see in Fig. 4(c), this corresponds to the HOMO-LUMO excitation transferring an electron from

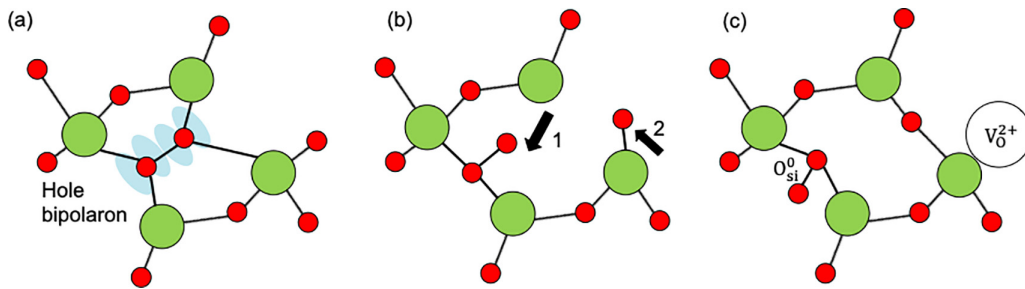


FIG. 2. Schematic diagram illustrating FP creation in β -Ga₂O₃. (a) Formation of a hole bipolaron, which creates a peroxide O–O bond. (b) Transition state of FP formation, with arrows indicating the following: step (1) displacement of the O–O dimer into a split-interstitial (O_{si}^0) and step (2) oxygen displacement leading to the formation of V_O^{2+} . (c) Final structure of the FP. Green spheres represent Ga atoms, while red spheres indicate O atoms.

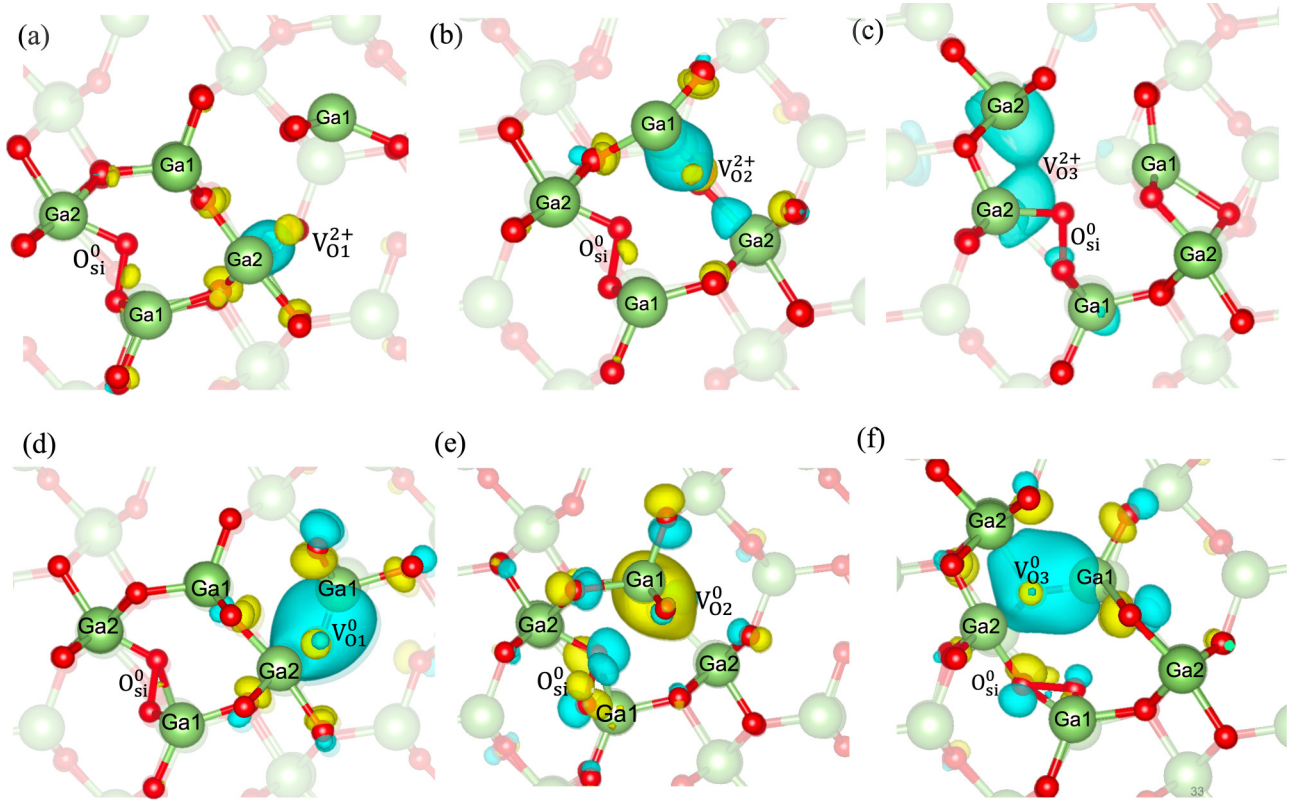


FIG. 3. FP structures corresponding to $V_{O1}^{2+} + O_{si}^0$ (a), $V_{O2}^{2+} + O_{si}^0$ (b), $V_{O3}^{2+} + O_{si}^0$ (c), $V_{O1}^0 + O_{si}^0$ (d), $V_{O2}^0 + O_{si}^0$ (e), and $V_{O3}^0 + O_{si}^0$ (f). Isosurfaces represent the LUMO (a)–(c) and HOMO (d),(e) states at an isovalue of 0.015. Green spheres represent Ga atoms, while red spheres indicate O atoms.

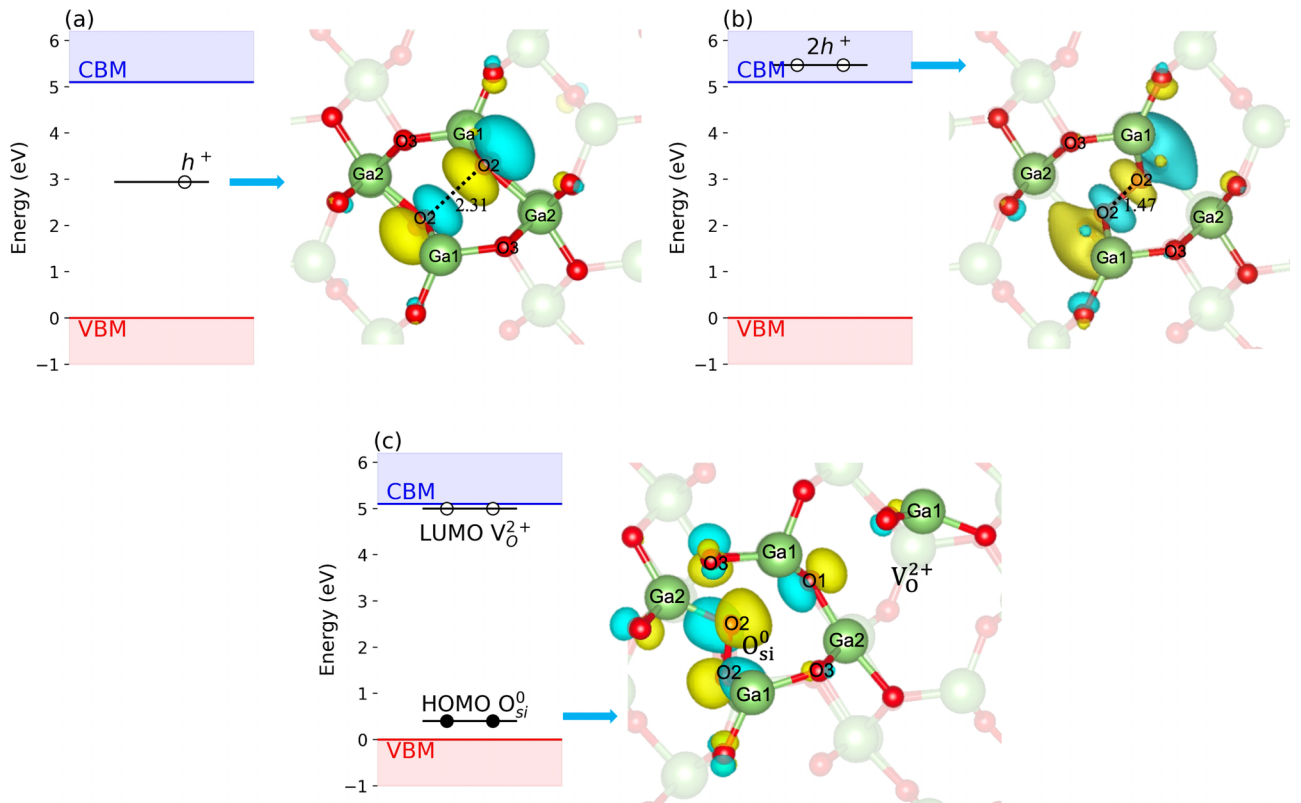


FIG. 4. KS levels and corresponding wave functions of β -Ga₂O₃ at an isovalue of 0.04 calculated using PBE0-TC-LRC. (a) STH on O₂; (b) hole bipolaron; (c) FP: $O_{si}^0 + V_{O1}^{2+}$. Green spheres represent Ga atoms, while red spheres indicate O atoms.

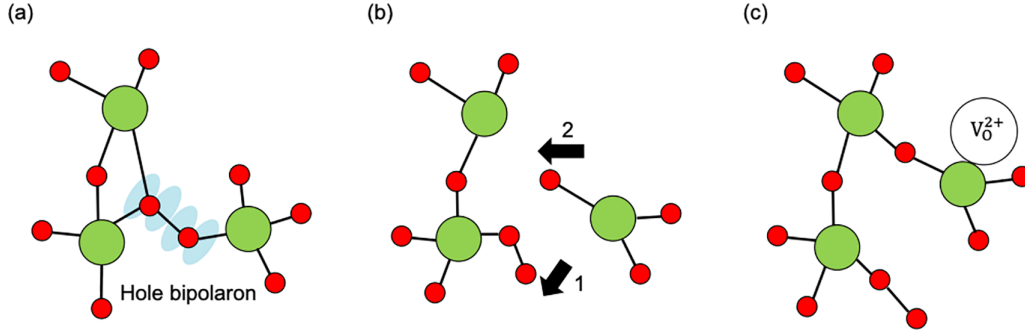


FIG. 5. Schematic diagram illustrating Frenkel pair (FP) creation in a-Ga₂O₃. (a) Formation of a hole bipolaron. (b) Transition state for FP creation, with arrows indicating significant atomic relaxations leading to the formation of (1) O_{si}^0 and (2) V_O^{2+} . (c) Final structure of the FP. Green spheres represent Ga atoms, while red spheres indicate O atoms.

O_{si}^0 into the vacancy. However, the initial configuration was found to be energetically more favorable, with relative energies lower by 1.67 eV, 1.06 eV, and 2.06 eV using PBEsol for the $V_{O1}^{1+} + O_{si}^{1+}$, $V_{O2}^{1+} + O_{si}^{1+}$, and $V_{O3}^{1+} + O_{si}^{1+}$ configurations, respectively. To further understand the electronic contributions to the creation of FP, the Kohn-Sham (KS) energy levels of the STH, bipolaron, and FP structures were plotted in Fig. 4. When a hole becomes trapped on the O2 atoms in β -Ga₂O₃, two O2 atoms localize a hole as a two-center STH, as reported in Refs. [26,27,29,59]. The STH contributes to the KS level at around 2.9 eV with respect to the VBM, as seen in Fig. 4(a). Once the second hole is injected, forming a hole bipolaron as an O–O dimer, the KS level shifts to above CBM at around 0.5 eV, as shown in Fig. 4(b). When the FP structure is formed, the O–O dimer subsequently becomes an O_{si}^0 , which contributes to the HOMO level slightly above the VBM, while the LUMO level is contributed by the V_O^{2+} near the CBM. This KS level of FP is similar to the KS of O_{si}^0 and V_O^{2+} , as reported in previous works [52,60]. During the transition from the bipolaron to the FP state, the KS level associated with the O–O dimer shifts from an unoccupied level above the CBM to a HOMO level near the VBM. This shift is attributed to the breaking of the O2–Ga1 bond in the bipolaron structure, leading to the formation of the FP configuration ($V_{O1}^{2+} + O_{si}^0$), as illustrated in Fig. 4(c). The original projected density of states (PDOS) data for the O–O dimer, on which the schematics in Fig. 4 are based, are given in Fig. S2.

The created FPs can either separate further via diffusion of O vacancy and/or interstitial or recombine back, restoring the lattice. The probabilities of these processes are determined by the corresponding barriers. Barriers for the neutral oxygen interstitial diffusion are approximately 1.0 eV, as described in [52]. Barriers for O vacancy diffusion are discussed below. In Table I, we also present the recombination barriers (E_b^r) for the NN FPs. FPs formed in pristine lattice exhibit significantly lower recombination barriers (below 0.5 eV), indicating that they can easily recombine and restore the pristine structure.

B. Formation of Frenkel pairs in a-Ga₂O₃

In a-Ga₂O₃, similar to the crystalline β phase, we observed that the second hole can be trapped to form a hole bipolaron, which leads to the elongation of nearby Ga–O bonds, as illustrated in Fig. 5(a) and previously discussed in Ref. [29].

Following the analogy with β -Ga₂O₃, a similar mechanism of FP formation was considered in a-Ga₂O₃, as shown in Fig. 5.

The eight FP structures produced are listed in Table II. All reactions are endothermic. The energy barriers for FP formation (E_b^f) range from 1.24 to 2.61 eV, while the recombination barriers (E_b^r) range from 0.10 to 1.16 eV. On average, the forward barrier is 2.05 eV and the recombination barrier is 0.62 eV, both lower than those observed in β -Ga₂O₃. Similar distinct relaxation processes involving two oxygen atoms, leading to the formation of O_{si}^0 and V_O^{2+} to form the FP structure, were identified in amorphous samples. The calculated displacements of these two atoms are presented in Table II as D1 and D2, respectively. The FP defect creation mechanism was also previously found in HfO₂ with barriers between 1.1 and 3 eV [33,46].

C. V_O^{2+} migrations in β and a-Ga₂O₃

After the formation of nearest-neighbor (NN) FPs, V_O^{2+} can migrate in an electric field and create a separate defect pair. Therefore, calculations were carried out to investigate this migration. The migration barriers are presented in Table III. Relative energy profiles with respect to the initial

TABLE II. Parameters describing the FP formation in four a-Ga₂O₃ samples with the bipolaron binding energy (BE) in eV for a-Ga₂O₃ + 2h⁺ (hole bipolaron) $\rightarrow$ $V_O^{2+} + O_{si}^0$ reaction. E_{rel} is the energy relative to the initial state (eV), E_b^f and E_b^r are the forward and recombination barriers (eV), and D1, D2 are the O–O atomic displacements (Å) for dimer formation and V_O formation, respectively, calculated using CI-NEB with PBEsol.

Sample	BE ^a	V _O site	E _{rel}	E _b ^f	E _b ^r	D1	D2
1	0.31	1	1.45	2.61	1.16	2.03	2.50
		2	1.80	1.93	0.13	1.86	2.09
2	0.70	1	0.54	1.34	0.79	1.33	4.04
		2	1.57	2.32	0.75	2.82	3.37
3	0.32	1	1.03	1.24	0.21	2.60	1.68
		2	1.14	1.24	0.10	2.63	1.99
4	0.48	1	1.76	2.36	0.60	2.60	2.42
		2	1.28	2.00	0.72	2.47	0.73
Average			1.43	2.05	0.62		

^aFrom Ref. [52].

TABLE III. Parameters of the V_O^{2+} migration in FP structure $V_O^{2+} + O_{si}^0$ for β - and α -Ga₂O₃: relative energy (E_{rel}) with respect to the initial FP structure, forward barriers (E_b^f), recombination barriers (E_b^r) in eV, and atomic displacements of O to migrate V_O^{2+} to a new site in Å, using CI-NEB with PBEsol.

FP structure	Migration path	E_{rel}	E_b^f	E_b^r	Displacement
β -Ga ₂ O ₃ $V_{O1}^{2+} + O_{si}^0$	1: V_{O1} to V_{O1}	-0.09	1.31	1.40	2.90
	2: V_{O1} to V_{O2}	1.00	1.71	0.71	2.93
	3: V_{O1} to V_{O3}	-0.02	1.66	1.68	2.67
	1: V_{O2} to V_{O1}	-0.80	1.08	1.88	2.89
	2: V_{O2} to V_{O2}	0.10	2.13	2.03	2.95
	3: V_{O2} to V_{O3}	-0.78	1.13	1.91	2.81
α -Ga ₂ O ₃ $V_{O3}^{2+} + O_{si}^0$	1: V_{O3} to V_{O1}	0.70	1.58	0.88	2.65
	2: V_{O3} to V_{O2}	1.73	2.28	0.55	2.92
	3: V_{O3} to V_{O3}	1.00	2.73	1.73	2.54
α -Ga ₂ O ₃ Sample 1	Path1	0.06	0.49	0.43	1.54
	Path2	0.35	0.75	0.40	1.77
	Path3	0.34	0.87	0.53	1.94
α -Ga ₂ O ₃ Sample 2	Path1	0.17	0.62	0.45	2.26
	Path2	0.86	1.27	0.41	3.07
	Path3	0.17	0.65	0.48	1.73
	Average	0.33	0.78	0.45	2.05

FP structures are also shown in Figs. S3 and S4 [58] for β and α -Ga₂O₃, respectively.

Migration barriers for V_O^{2+} in the β phase vary between 1.08 and 2.73 eV, depending on the specific migration sites. In particular, the barriers for migrations from V_{O2}^{2+} to a new V_{O2}^{2+} , from V_{O3}^{2+} to a new V_{O3}^{2+} , and from V_{O3}^{2+} to V_{O2}^{2+} are relatively high, exceeding 2 eV, indicating that these paths are energetically less favorable. In contrast, migration to V_{O1}^{2+} sites exhibits lower barriers. These results confirm earlier studies using DFT with the PBE functional, which suggested that migration to V_{O1}^{2+} sites requires a lower energy barrier compared to other paths [61]. The displacements of the O atoms participating in the migration of V_O^{2+} are shown in Table III, with an average of around 2.8 Å, which is close to the O—O distance in β -Ga₂O₃.

In the amorphous phase, the migration of V_O^{2+} was systematically explored for two FP structures in samples 1 and 2. For each FP structure, three distinct migration pathways are sampled. The migration barriers for these paths are listed in Table III, with values ranging from 0.49 to 1.27 eV; in contrast, the recombination barriers are between 0.40 and 0.53 eV. Notably, the average V_O^{2+} migration barrier in α -Ga₂O₃ is determined to be lower, at approximately 0.78 eV, compared to that in the β -Ga₂O₃. In the amorphous structure, the displacements of oxygen during V_O^{2+} migrations average approximately 2.0 Å, which is considerably smaller than in the crystalline phase. This indicates that structural flexibility significantly impacts the dynamics of defects in amorphous materials. The lower migration barriers and the decreased atomic displacements in α -Ga₂O₃ suggest that, once a FP forms, V_O^{2+} ions can migrate more easily to adjacent oxygen sites compared to the more rigid crystalline phase.

IV. DISCUSSION AND CONCLUSIONS

We investigated whether hole trapping facilitates Frenkel pair creation in β -Ga₂O₃ and α -Ga₂O₃ using the DFT calculations with functional PBEsol. This work was motivated by previous results that hole trapping occurs in both the amorphous and crystalline phases. Although a hole polaron has a large trapping energy of around 0.5–0.8 eV [26,27,59,62,63], it can hop between other sites with an activation energy of around 0.24–0.74 eV, depending on the sites, as shown using the NEB calculation with DFT + U [63]. Therefore, under negative bias stress (NBS) or negative bias and illumination stress (NBIS), hole polarons can form and then react with a second hole, forming hole bipolarons [29]. The hole bipolaron is characterized by the formation of an O—O dimer, which weakens and distorts the Ga—O bonds.

In this work, we show that this significantly reduces barriers for creation of NN FPs of O vacancy (V_O^{2+}) and O interstitial (O_{si}^0). In the β phase, the energy barriers for FP formation range between 3.47 and 4.80 eV, depending on the local environment. However, in the amorphous phase, both the reaction enthalpies and barriers are much lower, making FP formation via hole trapping more favorable compared to the β phase. Moreover, it was found that the migration barriers for V_O^{2+} to escape from NN FP structures are lower in the amorphous phase than in the crystalline phase. This can promote easier migration under the influence of an external electric field. However, the vacancy-interstitial recombination barriers are comparable and often lower than the defect separation barriers. Therefore, we do not expect this mechanism to be very efficient overall. However, it can be expected to be much more efficient in amorphous rather than in crystalline films.

We note that when injected or excited electrons are also present, these can be trapped by interstitial O atoms forming interstitial O^{2-} ions. Previous calculations [52,53] show that these ions have much smaller diffusion barriers along the [010] direction (0.12–0.15 eV) than split-interstitial atoms. This can create the second efficient channel for separation of FPs and increase the number of stable defects.

We note that the strong reduction of FP formation barriers was also predicted in α -HfO₂ under electron injection [33,64] and hole injection [33]. The mechanism proposed here can contribute to radiation-induced degradation of devices where hole injection can take place under stress conditions, such as radiation stress from x rays or photons in detectors. In MOSFETs, where Ga₂O₃ serves as an n -channel, degradation may occur when subjected to NBS with high voltage. Under these conditions, hole bipolarons can also contribute to threshold voltage shifts. In resistive random access memory devices, where Ga₂O₃ serves as a dielectric, this mechanism can contribute to resistive switching by creating O vacancies. The existence of such vacancies is implied [14,15,65] but the mechanism of their creation is not established.

To summarize, our study provides possible mechanisms which can be responsible for the degradation of Ga₂O₃-based devices under hole injection conditions, such as under irradiation NBIS, which can damage photo- and x-ray detectors [41,66]. It expands the number of oxides where trapping of carriers has been predicted to contribute to structural changes, such as SiO₂, HfO₂, and Al₂O₃ [36,43,45,46,67–69].

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DATA AVAILABILITY

The data that support the findings of this article are openly available [71].

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