Linking Diffusion Kinetics to Defect Electronic Structure in Metal Oxides: Charge-Dependent Vacancy Diffusion in Alumina

Yinkai Lei and Guofeng Wang*

Department of Mechanical Engineering and Materials Science, University of Pittsburgh,
Pittsburgh, PA 15261, USA

* Correspondence should be sent to guw8@pitt.edu

Abstract

We study the diffusion of charged vacancies in α -Al₂O₃ crystal using the first-principles calculation method. We predict that the migration energy for vacancy diffusion strongly depends on the charge state of the vacancy involved. Importantly, we reveal that this charge-dependent vacancy diffusion is directly related to the electron occupancy and energy level change of the defect states of the charged vacancy in alumina. Hence, our study establishes a direct link between the diffusion kinetics and electronic structure of metal oxides.

Keywords: α -Al₂O₃; Vacancy; Diffusion; First-principles;

Understanding the static and dynamic behavior of point defects in metal oxides is essential for optimization of electrical, optical, and mechanical functions of these materials [1, 2]. In this letter, we used the first-principles density functional theory (DFT) calculation method to unveil the physical origin of the charge-dependent atom/vacancy diffusion in alumina (α -Al₂O₃). The dependence of atom/vacancy mobility on its electric charge state has direct implication for the growth kinetics of protective alumina scales on high-temperature alloys [3] and the functional performance of alumina in a resistive random-access-memory (ReRAM) device [4].

In this study, the formation energy and migration energy of charged vacancies in alumina were calculated using the DFT calculations with the projector augmented wave method [5] and the Perdew-Burke-Ernzerhof exchange-correlation functional [6], as implemented in the Vienna Ab initio Simulation Package (VASP) [7,8]. In all these DFT calculations, we used a kinetic energy cutoff of 500 eV. The α -Al₂O₃ bulk crystal was modeled with a 2×2×1 supercell of conventional hexagonal cell lattice (shown in Fig. 1(a)). Without vacancy defects, there are in total 48 Al atoms and 72 O atoms in our simulation cell. We used a 3×3×2 Monkhorst-Pack k-point mesh [9] for k-space integration in our DFT calculations. A charged vacancy in α -Al₂O₃ was generated by removing an atom from the supercell and changing the total number of electrons in the supercell as required. In this work, we investigated the formation energy and mobility of the O vacancy with a charge of 0 (V_O^0), +1 (V_O^{1+}), or +2 (V_O^{2+}) and the Al vacancy with a charge of 0 (V_{Al}^0), -1 (V_{Al}^{1-}), -2 (V_{Al}^{2-}), or -3 (V_{Al}^{3-}). All the crystal structures were optimized under constant-volume restriction until the Hellman-Feynman force exerted on each ion is less than 0.01 eV/Å.

The formation energy (ΔE_f) of a vacancy with a charge of q in alumina can be calculated as follows [10]:

$$\Delta E_f = E^{def,q} - E^{perf} + \mu_i + q\mu_e \quad (1)$$

where $E^{def,q}$ is the energy of the relaxed simulation cell containing the charged vacancy whereas E^{perf} is the energy of the perfect crystal; μ_i is the chemical potential of the Al or O atom removed from alumina crystal; In this study, μ_i was calculated following the scheme suggested in Ref. [10] and using the DFT results and experimental data [11] as inputs; μ_e is the chemical potential of an electron in alumina. When calculating $E^{def,q}$, we have corrected the finite size error introduced by periodic charges following the established schemes [12]. The electron chemical potential μ_e has been calculated as a summation of the valence-band maximum (E_{VBM}) of the perfect crystal and a Fermi level ε_F (whose value is zero at VBM). In this study, E_{VBM} was taken as an energy difference between the bulk alumina with 0 and 1+ charge and ε_F was calculated by enforcing the requirement of charge neutrality in the crystal [13].

It notes that the Fermi level ε_F of alumina crystal affects the stability of charged vacancies and can be tuned by changing the concentration of aliovalent dopants. We found from our DFT calculations that V_O^0 would be the most stable O vacancy when ε_F is greater than 2.58 eV whereas V_O^{2+} would be the most stable O vacancy when ε_F is below 2.58 eV. Regarding various charged Al vacancies, our DFT results predicted that the stable region of ε_F for V_{Al}^0 , V_{Al}^{1-} , V_{Al}^{2-} , and V_{Al}^{3-} was from 0.0 eV (i.e., E_{VBM}) to 0.25 eV, from 0.25 eV to 0.82 eV, from 0.82 eV to 1.49 eV, and greater than 1.49 eV, respectively. Our predictions agree with the previous results attained by Hine *et al* [10]. It should be pointed out that the self-interaction error of DFT could lead to underestimation of the formation energy of V_O^0 and V_O^{1+} [10]. Consequently, our DFT predictions on the stability of various O vacancies are in a qualitative (not quantitative) nature. At an example condition of $T=1300$ K and $p_{O_2}=0.2$ atm, ε_F was calculated to be 1.93 eV in an un-doped alumina crystal. Thus, the stable vacancies are predicted to be V_O^{2+} for O vacancy and

V_{Al}^{3-} for Al vacancy in intrinsic Al_2O_3 crystal at such a condition. Introducing n-type dopants to alumina crystal leads to an increase in ε_F , which could make V_{O}^0 more likely to occur. In contrast, increasing p-type doping level might increase the concentration of V_{Al}^{2-} , V_{Al}^{1-} , and V_{Al}^0 of Al vacancies in $\alpha\text{-Al}_2\text{O}_3$.

Inside bulk alumina crystal (shown in Fig. 1(a)), we have identified four distinct elementary paths for O atom-vacancy exchange (shown in Fig. 1(b)) as well as four distinct elementary paths for Al atom-vacancy exchange (shown in Fig. 1(c)) [14]. For each of these diffusive jumps, we determined the minimum energy path (MEP) of the migrating vacancy with different charge states using the climbing image nudged elastic band method [15] and further verified the transition state (which should have only one imaginary vibrational mode) with vibrational frequency calculations. Moreover, we calculated the migration energy for each diffusive jump and presented our calculation results in Table 1. We find that the MEP of the jumps $\text{Al}_2\text{-Al}_4$ and $\text{Al}_3\text{-Al}_4$ contains a locally minimum-energy configuration and thus could be further divided into two diffusive segments. It is worth pointing out that our calculated value of 3.57 eV for the migration barrier of V_{O}^0 along the $\text{O}_1\text{-O}_2$ path is in good agreement with previous DFT calculation of 3.70 eV for the same path [16]. Importantly, our DFT results in Table 1 revealed that the vacancy diffusion in alumina crystal strongly depends on the charge state of the vacancy involved.

In order to understand this charge-dependent vacancy diffusion, we have analyzed the electronic structure of the migrating charged vacancies in alumina crystal. As discussed in previous electronic structure calculations [17], the valence band of perfect alumina is just the O 2p band near the valence-band maximum whereas the conduction band is mainly composed of Al 3s and 3p bands. Moreover, extra defect states could be observed inside the band gap if there are

vacancies in the alumina crystal. In this study, we found in $\alpha\text{-Al}_2\text{O}_3$ that the defect state associated to the O vacancy was located at 2.41 eV above E_{VBM} and composed of the 3s and 3p orbitals from the nearest-neighboring Al atoms (illustrated in Fig. 2(a-b)). The defect states associated to the Al vacancy was found to posit at 0.58 eV above E_{VBM} and composed of the 2p orbitals from the nearest-neighboring O atoms (illustrated in Fig. 3(a-b)). Comparing the electronic structures of the O vacancy at its relaxed state (Fig. 2(a-b)) and its transition state of jump $\text{O}_1\text{-O}_2$ (Fig. 2(c-d)), we noticed that the energy level of the defect state shifted up by 1.51 eV at the transition state accompanying to the spreading of defect electron density from one local Al tetrahedron to the two neighboring Al tetrahedrons. Examination of the other O vacancy diffusion paths yields the similar results. It is apparent that the O vacancy diffusion through alumina crystal involves an upshift of the energy level of the defect state (composed of Al 3s and 3p bands) toward the conduction band of the crystal. Regarding to the Al vacancy diffusion in $\alpha\text{-Al}_2\text{O}_3$, Fig. 3 shows that the energy level of the defect states (composed of O 2p band) actually shift down toward the valence band of the crystal at the transition state in which the defect electron density is evenly distributed between the two neighboring O octahedrons.

The migration energy for vacancy diffusion can be considered as the sum of the energy changes of the electrons occupying the valence band of the crystal and those of the electrons occupying the vacancy defect states in the diffusion process. The total number of the electrons occupying the valence band of the crystal does not change with the charge state of the vacancies. However, the electron occupancy on the defect states would vary greatly with variations of the vacancy charge. The number of electrons in the defect states can be calculated by integrating the DOS from VBM to the maximum occupied energy level as marked in Figs. 2 and 3. For the O vacancy in alumina, the defect state is unoccupied for V_0^{2+} , singly occupied for V_0^{1+} , and doubly

occupied for V_O^0 (as marked in Fig. 2(b-d)). For the Al vacancy in alumina, the defect states consist of two very close energy levels and contain no electron for V_{Al}^0 , one electron for V_{Al}^{1-} , two electrons for V_{Al}^{2-} , and three electrons for V_{Al}^{3-} (as marked in Fig. 3(b-d)). Neglecting the energy change related to valence electrons of the crystal, the calculated diffusion migration energy difference between the vacancies with different charges should be approximately equal to a multiplication of the electron occupancy by the energy shift of the defect states for the same diffusive path. Indeed, our results in Fig. 4 exhibited good linear relation between the change in the diffusion migration energy due to the vacancy charge and the change in the defect state energy level during the vacancy diffusion. Importantly, it was shown that the slope of these linear relations were just the difference in electron occupancy on the defect states of the charged vacancies. Therefore, we uncover in this study that the energy shift in the electronic defect states during diffusion is mainly responsible for the observed charge-dependent vacancy diffusion in alumina. The small deviation of our calculation data from the reference straight lines (which all pass point (0, 0)) in Fig. 4 implies that the changes in valence electron energy during the diffusion of the charged vacancies are comparably less pronounced.

Understanding the origin of the charge-dependent vacancy diffusion helps us to fully comprehend the diffusion processes in alumina [18]. Using our calculated migration energies in Table 1, we performed the Kinetic Monte Carlo (KMC) simulations based on the harmonic transition state theory [19] to evaluate the diffusivity of O and Al atoms through exchanging with charged vacancies in Al_2O_3 crystal in the temperature range of 1300 K to 1800 K. From the Arrhenius plot of our calculated diffusion coefficients, we predicted that the activation energy for the O diffusion through exchanges with V_O^0 , V_O^{1+} , and V_O^{2+} was 11.91 eV, 9.49 eV, and 7.21 eV, respectively. The activation energy for the Al diffusion through exchanges with V_{Al}^0 , V_{Al}^{1-} , V_{Al}^{2-} ,

and V_{Al}^{3-} was found to be 4.76 eV, 3.57 eV, 2.98 eV, and 2.99 eV, respectively. In addition, our results indicated that the prefactor of the O diffusion through V_{O}^{2+} had a smaller value than through the other possible charged O vacancies whereas the prefactor of the Al diffusion through V_{Al}^{3-} had the largest value among all the possible charged Al vacancies. In summary, we found that V_{O}^{2+} and V_{Al}^{3-} vacancies respectively led to the fastest diffusion of O and Al in alumina. In particular, our predicted activation energy (7.21 eV) and prefactor ($3.27 \times 10^{-4} \text{ m}^2/\text{s}$) for O diffusion through V_{O}^{2+} fall well into the range of experimental values summarized in Ref. [18].

Linking diffusion kinetics to defect electronic structure offers a new perspective to understand the reactive element (RE, such as Hf, Zr and Y) effect in reducing the growth rate of Al_2O_3 scale. Conventionally, the RE effect is explained as a geometric blockage to the Al diffusion by the segregated RE atoms along grain boundaries [20]. More recently, Heuer et al suggested that the change in the electronic structure of Al_2O_3 introduced by REs had crucial roles in affecting alumina scale formation [21]. In this study, we calculated the binding between a Hf atom (substituting a Al atom) and a Al vacancy (with different charges) in Al_2O_3 and examined how the doped Hf atom affects the defect electronic structure of the neighboring Al vacancy. Among all the possibilities of charge, we found that it was most energetically favorable for the doped Hf to bind with a V_{Al}^{3-} at its nearest neighbor site. The binding energy between Hf and V_{Al}^{3-} was predicted to be 1.70 eV, suggesting strong attraction of the two point defects. More relevantly, we found that the existence of Hf dopant increased the migration energy for neighboring V_{Al}^{3-} diffusion along path $\text{Al}_1\text{-Al}_2$ from 1.55 eV to 1.93 eV. Further electronic structure analysis reveals that the Hf dopant modifies the energy shift of the vacancy defect states during the diffusion and introduces a 0.12 eV increase (32% of the total increase) in the migration energy of the vacancy. Hence, our DFT results indicate that the RE effect in reducing

Al diffusion rate in Al_2O_3 could be partially attributed to the electronic structure modification in vacancy defect states.

In this letter, we presented our DFT calculation results on the formation and diffusion of vacancies with different charge states in $\alpha\text{-Al}_2\text{O}_3$ bulk crystal. We predicted that the migration energy for the vacancy diffusion varied greatly with the change in the vacancy charge. Further analysis reveals that the observed charge-dependent vacancy diffusion is the result of the similar energy shift but different electron occupancy of the defect states associated with the differently charged vacancy during the diffusion. This work provides a new view on the diffusion processes in alumina, suggesting a novel route for controlling the diffusion kinetics by tuning the charge state of the vacancies. Our finding about the charge-dependent vacancy diffusion should be applicable to a broad range of metal oxide ceramics.

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References

- [1] S.V. Kalinin and N.A. Spaldin, *Science* 341 (2013) 858.
- [2] H.L. Tuller and S.R. Bishop, *Annu. Rev. Mater. Res.* 41 (2011) 369.
- [3] A.H. Heuer, T. Nakagawa, M.Z. Azar, D.B. Hovis, J.L. Smialek, B. Gleeson, N.D.M. Hine, H. Guhl, H.S. Lee, P. Tangney, W.M.C. Foulkes, and M.W. Finnis, *Acta Materialia* 61 (2013) 6670.
- [4] M.Y. Yang, K. Kamiya, B. Magyari-Kope, M. Niwa, Y. Nishi, and K. Shiraishi, *Appl. Phys. Lett.* 103 (2013) 093504.
- [5] G. Kresse and D. Joubert, *Phys. Rev. B* 59 (1999) 1758.
- [6] J.P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* 77 (1996) 3865.
- [7] G. Kresse and J. Hafner, *Phys. Rev. B* 47 (1993) 558.
- [8] G. Kresse and J. Furthmuller, *Compt. Mater. Sci.* 6 (1996) 15.
- [9] H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* 13 (1976) 5188.
- [10] N.D.M. Hine, K. Frensch, W.M.C. Foulkes, and M.W. Finnis, *Phys. Rev. B.* 79 (2009) 024112.
- [11] R. C. Weast, ed., *CRC Handbook of Chemistry and Physics*, 69th Edition, 1988-1989, CRC Press, Inc.
- [12] G. Makov and M.C. Payne, *Phys. Rev. B* 51 (1995) 4014.
- [13] R. Sun, M. K. Y. Chan, S. Y. Kang, and G. Ceder, *Phys. Rev. B.*, 84 (2011) 035212.
- [14] Y. Lei, Y. Gong, Z. Duan, and G.F. Wang, *Phys. Rev. B* 87 (2013) 214105.
- [15] G. Henkelman, B.P. Uberuaga, and H. Jónsson, *J. Chem. Phys.* 113 (2000) 9901.
- [16] J. Carrasco, N. Lopez, and F. Illas, *Phys. Rev. Lett.*, 93 (2004) 225502.
- [17] K. Matsunaga, T. Tanaka, T. Yamamoto, and Y. Ikuhara, *Phys. Rev. B* 68 (2003) 085110.
- [18] A.H. Heuer, *J. Euro. Ceram. Soc.*, 28 (2008) 1495.

- [19] G. H. Vineyard, J. Phys. Chem. Solids, 3 (1957) 121-127.
- [20] B. A. Pint, K. B. Alexander, J. Electrochem. Soc., 145 (1998) 1819-1829.
- [21] A.H. Heuer, D.B. Hovis, J.L. Smialek, and B. Gleeson, J. Am. Ceram. Soc. 94 (2011) S146.

TABLE 1. Calculated migration energy for charged O and Al vacancy diffusion in α -Al₂O₃ lattice. For the Al₂-Al₄ and Al₃-Al₄ diffusion paths, we present the migration energies for both of the two separate diffusion segments. Zero point energy correction is included in the migration energy by calculating the vibrational frequencies of the vacancies and their transition states.

O vacancies	O₁-O₂	O₁-O₃	O₁-O₄		O₃-O₄	
V_O^0	3.57	4.07	4.70		5.02	
V_O^{1+}	2.06	2.78	3.09		3.64	
V_O^{2+}	0.91	1.79	1.75		2.65	
Al vacancies	Al₁-Al₂	Al₁-Al₃	Al₂-Al₄		Al₃-Al₄	
			Step1	Step2	Step1	Step2
V_{Al}^0	1.78	2.07	1.53	1.64	1.91	0.32
V_{Al}^{1-}	1.73	2.07	1.48	1.64	1.87	0.31
V_{Al}^{2-}	1.66	1.98	1.29	1.67	1.74	0.27
V_{Al}^{3-}	1.55	1.79	1.01	1.78	1.56	0.25

Figure Captions:

Figure 1. (a) Conventional hexagonal unit cell of the crystal structure of α -Al₂O₃. Schematics of various paths (delineated with black arrows) for (b) O vacancy and (c) Al vacancy to diffuse through the alumina bulk crystal. In the figure, the red balls represent O atoms and the gray balls represent Al atoms.

Figure 2. 3D isosurface (isovalue of 0.015) of electron density and calculated densities of states (DOS) associated to the defect state of O vacancy in α -Al₂O₃ at (a, b) the relaxed state and (c, d) the transition state of diffusive path O₁-O₂. The DOSs of Al, Al_I, and Al_{II} are those from all the six surrounding Al atoms, the two Al atoms adjacent to the relaxed O vacancy, and the two Al atoms farther away from the relaxed O vacancy.

Figure 3. 3D isosurface (isovalue of 0.050) of electron density and calculated densities of states (DOS) associated to the defect states of Al vacancy in α -Al₂O₃ at (a, b) the relaxed state and (c, d) the transition state of diffusive path Al₁-Al₂. The DOSs of O, O_I, and O_{II} are those from all the ten surrounding O atoms, the four O atoms adjacent to the relaxed Al vacancy, and the four O atoms farther away from the relaxed Al vacancy.

Figure 4. The calculated difference in diffusion migration energy for (a) O vacancies and (b) Al vacancies with different charges as a function of the energy shift (ΔE_V) of the defect state (with a single electron occupancy) for the corresponding diffusive paths. The dashed lines are used to guide the eyes and show linear relations with specified slopes.

Figure 1, Lei et al

Figure 2, Lei et al

Figure 3, Lei et al

Figure 4, Lei et al