

Supplementary Materials

Investigation of thermal stability and reactivity of Rh nanoclusters on a thin film of Al₂O₃/NiAl(100)

Zhen-He Liao¹, Po-Wei Hsu¹, Ting-Chieh Hung¹, Guan-Jr Liao¹, Zhao-Ying Chern², Yu-Ling Lai³, Li-Chung Yu³, Yao-Jane Hsu³, Jeng-Han Wang², Peilong Chen¹ and Meng-Fan Luo^{1,*}

¹*Department of Physics, National Central University, 300 Jhongda Road, Jhongli 32001, Taiwan*

²*Department of Chemistry, National Taiwan Normal University, Taipei, Taiwan*

³*National Synchrotron Radiation Research Center, 101 Hsin-Ann Road, Hsinchu Science Park, Hsinchu 30076, Taiwan*

Method for DFT calculations

All the calculations for structural optimization and energetic calculation were performed using the Vienna Ab initio Simulation Package (VASP),¹⁻³ at the density functional theory

(DFT) level with a 3D periodic boundary condition. The exchange-correlation function was treated by the generalized gradient approximation⁴ with Perdew-Wang 1991 formulation (GGA-PW91).⁵ The electron-ion interaction was modeled by the projector-augmented wave method (PAW),^{6,7} combining the accuracy of augmented plane waves with the cost-effective pseudopotentials. The kinetic cutoff energy of plane-wave basis was set at 400 eV. The Brillouin-Zone (BZ) integration was sampled by Monkhorst-Pack scheme⁸ at 0.05×2 ($1/\text{\AA}$) interval in the reciprocal space. The structures and energies were optimized by quasi-Newton method with an energetic convergence of 1×10^{-4} eV and a gradient convergence of 1×10^{-2} eV. The transition states at the saddle points were located by Nudged Elastic Band (NEB) method⁴¹ at the same convergence criterions for activation energy (E_a) calculation.

Results

The DFT calculations were performed to derive the activation energies (E_a) for the Rh diffusion processes. The calculated E_a allow us to confirm that the relative rates of these various diffusion processes in the Monte Carlo simulation are reasonable. We computed the activation barrier (E_a) for a Rh single atom which diffuses on $\theta\text{-Al}_2\text{O}_3(100)$ surface, dissociates from and wags (diffusion along cluster edge) along the clusters on $\theta\text{-Al}_2\text{O}_3(100)$ surface. The models for the substrate of $\theta\text{-Al}_2\text{O}_3(100)$ were constructed by four

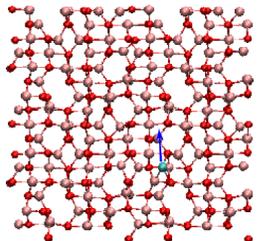
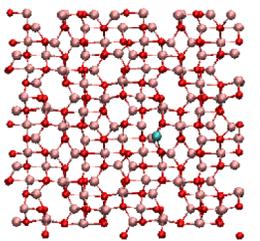
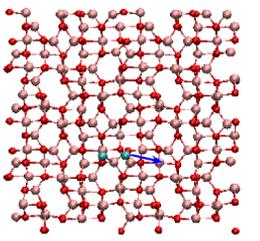
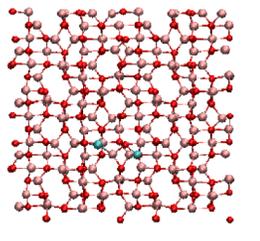
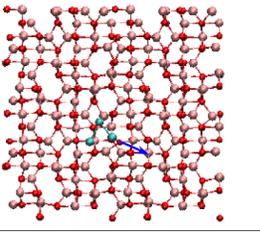
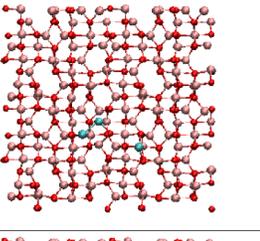
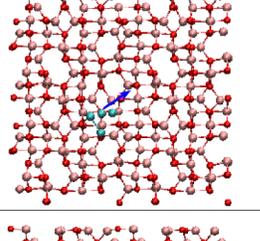
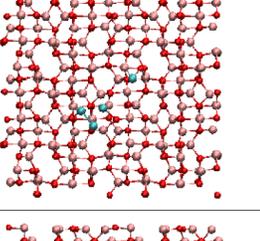
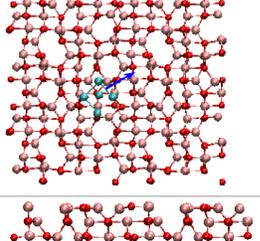
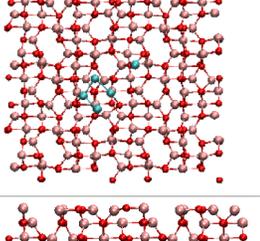
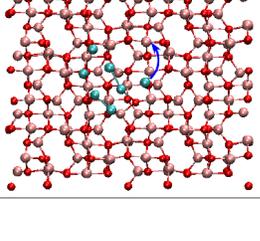
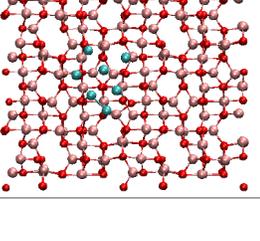
layers with the surface area of $23.64 \times 22.76 \text{ \AA}^2$ in a total of 128 Al and 192 O atoms; the bottom layer was fixed while top three ones were relaxed. The computed results show that a single Rh atom can easily diffuse on the $\theta\text{-Al}_2\text{O}_3(100)$ surface with a rather low E_a (0.33 eV); in the Monte Carlo simulation, such a hopping probability is one. The E_a for Rh atom dissociation from Rh₂ dimer and Rh₃ trimer in the triangular shape amount to 0.75 and 0.90 eV, respectively, indicating that the probabilities are declined by factors $e^{-0.42/kT}$ and $e^{-0.57/kT}$, respectively. In the Monte Carlo simulation, the probabilities become $e^{-\epsilon/kT}$ and $e^{-2\epsilon/kT}$. The hopping from the second layer and dissociating have $E_a = 0.86$ and 0.83 eV in the two cases (tetrahedral Rh₄ and pyramid Rh₅ in the figure), corresponding to the probabilities declined by factors $e^{-0.53/kT}$ and $e^{-0.50/kT}$; in the Monte Carlo simulation, the probabilities become $e^{-2\epsilon/kT}$ (the dissociation and descending from the upper to bottom layer are the critical processes respectively in tetrahedral Rh₄ and pyramid Rh₅). The relative rates of the kinetic processes in the Monte Carlo simulation may not precisely conform to the calculated activation energies, but the estimated relative values are reasonable. Finally, we computed the diffusion along the edge of an island. The calculated values were between 0 and 0.48 eV, depending on the position at which the atom was placed. The result indicates that the energetic barrier for the diffusion along the edge of an island is small and comparable to that on the oxide, which agrees with that in the Monte Carlo simulation the corresponding probability is one except that the atom crosses a corner.

References

1. Kresse, G.; Furthmüller, J., Efficient Iterative Schemes for Ab Initio Total-energy Calculations Using a Plane-wave Basis Set. *Phys. Rev. B* **1996**, *54* (16), 11169-11186.
2. Kresse, G.; Hafner, J., Ab Initio Molecular Dynamics for Liquid Metals. *Phys. Rev. B* **1993**, *47* (1), 558-561.
3. Kresse, G.; Hafner, J., Ab Initio Molecular-dynamics Simulation of the Liquid-metal-amorphous-semiconductor Transition in Germanium. *Phys. Rev. B* **1994**, *49* (20), 14251-14269.
4. Ceperley, D. M.; Alder, B. J., Ground State of the Electron Gas by a Stochastic Method. *Phys. Rev. Lett.* **1980**, *45* (7), 566-569.
5. Perdew, J. P.; Wang, Y., Accurate and Simple Analytic Representation of the Electron-gas Correlation Energy. *Phys. Rev. B* **1992**, *45* (23), 13244-13249.
6. Blöchl, P. E., Projector Augmented-wave Method. *Phys. Rev. B* **1994**, *50* (24), 17953-17979.
7. Kresse, G.; Joubert, D., From Ultrasoft Pseudopotentials to the Projector Augmented-wave Method. *Phys. Rev. B* **1999**, *59* (3), 1758-1775.

8. Monkhorst, H. J.; Pack, J. D., Special Points for Brillouin-zone Integrations. *Phys. Rev. B* **1976**, *13* (12), 5188-5192.
9. Mills, G.; Jonsson, H.; Schenter, G. K. *Surf. Sci.* **1995**, *324*, 305–337.

Figure 1

	Initial state	Final state	E_a (eV)
Rh diffusion			0.33
Rh dissociation from linear Rh₂			0.75
Rh dissociation from triangular Rh₃			0.90
Rh dissociation from tetrahedral Rh₄			0.86
Rh dissociation from pyramid Rh₅			0.83
Rh wagging from the plane Rh₇			0 ~ 0.48