Energy Calculation of Xenon Stability in Uranium Nitride Using Density Functional Theory

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1. Introduction

Several advanced nuclear fuels, with significantly improved properties compared to current commercial oxide fuels, are being investigated in the context of Generation-IV reactors. Uranium nitride is in particular generating a lot of interest owing to its superior thermophysical properties such as high thermal conductivity and high metal density [1].

The point defects are a major diffusion channel for fission gases. The defect and the mobility energies are needed to know the fission gas mobility in the point defect [2].

In this study, we investigated the stable position and mobility of representative fission gas Xe using the first-principles calculation implemented in the VASP (Vienna Ab initio Simulation Package) code.

2. Theory and Methods

We calculated the total energies using the VASP.4.6 code. All energy values were obtained based on the density functional theory (DFT) including the generalized gradient approximation (GGA), the projector-augmented-wave (PAW), and nudged elastic band (NEB) method.

2.1 Density functional theory (DFT)

DFT is a quantum mechanical method that is widely used to investigate the electronic structure of many-body systems, particularly molecules and condensed phases. DFT has been successfully applied to determine the properties of defects in solids, such as metals and semiconductors. These calculations most frequently rely upon periodic boundary conditions and plane-wave basis sets to simulated bulk materials in the presence of impurities [3].

2.2 Nudged elastic band (NEB) method

The NEB is a method for the calculation of saddle points and minimum energy paths between known reactants and products. The method is performed by optimizing a number of intermediate images along the reaction path. The lowest energy is obtained by each image while maintaining equal spacing to neighboring images. This constrained optimization is done by adding spring forces along the band between images and by projecting out the component of the force due to the potential perpendicular to the band [4].

2.3 Calculating details

The PAW method is applied to describe the electron-ion interaction. For the exchange and correlation energy of electrons, we have adopted a conventional GGA approach, because first-principle calculations to the GGA approximation showed almost correct energy information for UN, regardless of the fact that a wrong electronic band structure was predicted. Plane waves with a kinetic energy of up to 500 eV were used to expand the wave functions. The Monkhorst-Pack k-point scheme of a $2\times2\times2$ mesh was applied for the 64-atom supercell. For all the defect structures, ionic relaxation was performed, and the force acting on each ion was calculated until less than 0.01 eV/A. We applied a large super cell containing 64 atoms to decrease the defect-defect interactions.

We calculated the incorporation energy of Xe at defect sites, and obtained the migration energies of Xe, N vacancy, and U vacancy using NEB method.

2.3.1 Stability of Xenon in UN

We can determine the stability of fission products trapped at pre-existing trap sites using calculation incorporation energies. A comparison of incorporation energies is the simplest way by which fission product stability may be assessed. The incorporation energy is calculated according to

$$E_{Inc.} = E_{Xe} - (E_V + \mu_{Xe}) .$$

The incorporation energy $E_{Inc.}$ is defined as the energy required incorporating an atom at a pre-existing vacancy or interstitial site. E_{Xe} is the energy of the supercell containing Xe at a particular defect site, E_V is the energy of the supercell with a particular defect site, and μ_{Xe} is the energy of a single isolated atom of Xe.

3. Results

Table I shows the calculated results of incorporation energy. The Schottky defects were calculated along the [100] or the [111] direction.

Table I: Incorporation energies of Xe for U site, N site, and interstitial sites, and Schottky defects in [100] and [111] Miller indices lattice planes.

	N	U	Interstitial	[100]	[111]
UN	9,13	4.84	15.04	3.51	4.99

We calculated the atomic relaxation for the possible trapped positions of Xe at (a) N vacancy, (b) U vacancy, and (c) di-vacancy using the VASP code. Fig. 1 shows the results of atomic relaxation.

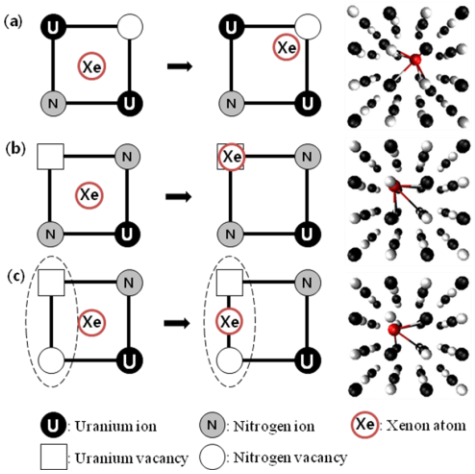

Fig. 1. The most stable positions of Xe in UN defect sites.

Fig. 2 shows the calculated migration energy using the NEB method. The migration energy is calculated from the system energy difference between the position of the ground state and the position of the excited state. The saddle point site and migration energy of Xe are shown in Fig. 3.

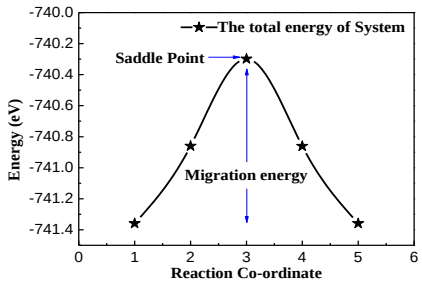

Fig. 2. The saddle points of Xe in system that is included U-di-vacancy.

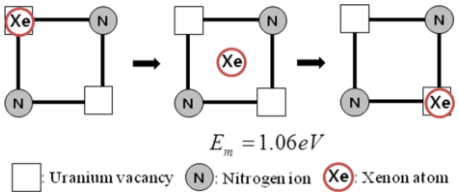

Fig. 3. The migration of Xe from a uranium vacancy to the next nearest uranium vacancy. The migration energy is calculated to be 1.06 eV using the NEB methods.

The migration energies of nitrogen and uranium vacancies are obtained to be 2.68 eV and 3.09 eV, respectively, and the saddle point of nitrogen and uranium are shown in Fig. 4.

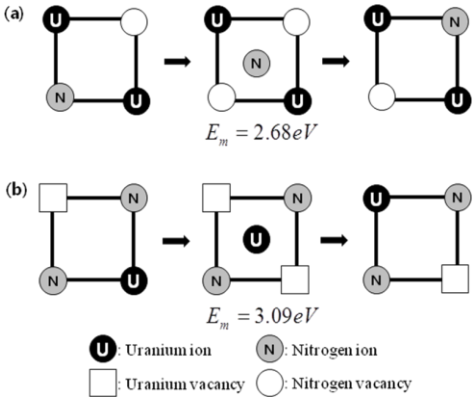

Fig. 4. The N-ion in (a) and the U-ion in (b) are moved to the other vacancy sites through the saddle point, respectively. The migration energies are 2.68 eV and 3.09 eV, respectively.

4. Conclusions

To find a stable site for Xe, we calculated the incorporation energies of Xe in various defects. The incorporation of Xe was more favorable through Schottky defect than a single vacancy defect. In particular, incorporation of the Schottky defects along the [100] direction was the most stable in this study.

In the case of Xe in an interstitial site, Xe atom flowed to the U vacancy and di-vacancy site by atomic relaxation. However Xe atom did not flow to the N vacancy because of the higher incorporation energy.

When Xe moves through uranium vacancies, its migration energy is 1.06 eV.

The uranium vacancy migration energy was much higher than the nitrogen vacancy migration energy. This means that the nitrogen ions are more movable than uranium ions through their vacancies. Thus, the migration of Xe is higher than the migration of lattice ions.

A future study needs to calculate the migration energy of Xe in a Schottky defect site.

REFERENCES

[1] M. Klipfel, P. Van Uffelen, J. Nucl. Mater. Vol. 422, pp.137-142, 2012.
[2] Hj. Matzke, Nucl. Appl. Vol 2, p131, 1966.
[3] W. Kohn, L. J. Sham, Phys. Rev. Vol. 140, pp.1133-1138, 1965.
[4] H. Jonsson, G Mills, K. W. Jacobsen, Classical and Quantum Dynamics in Condensed Phase Simulation edited by B.J. Berne, G. Ciccotti, and D. F. Coker, World Scientific, Singapore, p385, 1998.