Adsorption and Dissociation Mechanism of Excited N_2 on ZnSe Surface

Taketoshi Nakao and Takeshi Uenoyama

Central Research Laboratories,
Matsushita Electric Industrial Co., Ltd.
Moriguchi, Osaka 570, Japan

Nitrogen molecular adsorption and dissociation on ZnSe (100) surface has been studied by ab initio molecular orbital theory. Based on the electronic structure and energetics, the excited ($^3\Sigma_u^+$) nitrogen molecule can be selectively adsorbed and dissociated on a Zn atom of the ZnSe surface. This result supports the contention recently presented that the p-type ZnSe layers, which successfully realized blue-green lasers, are grown by the excited ($^3\Sigma_u^+$) nitrogen molecular beam from a plasma source.

I.   Introduction

Recently, Ohkawa et al. proposed that excited nitrogen molecules ($^3\Sigma_u^+$) are doped as shallow acceptors of ZnSe layer by molecular beam epitaxy, so called "radical doping method" [1]. Then, this doping method brought the realization of blue-green lasers made from II-VI compound semiconductors [2,3,4]. However, there is no microscopic studies of the mechanism how the excited nitrogen molecules are selectively doped in ZnSe layer as a p-type dopant. In the present paper, adsorption and dissociation of the ground and the excited nitrogen molecules on ZnSe (100) surface are investigated by ab initio molecular orbital theory for the first time and their mechanism are discussed from the electronic states.

II.   Models and calculations

For the calculations of the interaction between nitrogen molecules and ZnSe (100) surface, two kinds of cluster models shown in Fig. 1 are adopted. In each model, the ground state ($^1\Sigma_g^+$) and the excited state ($^3\Sigma_u^+$) are considered as a nitrogen molecule. The reason why ($^3\Sigma_u^+$) is chosen as a exited state is that its life time is much longer (2.0 seconds [4]) than that of the other excited states. Figure 1 (a) (1 (b)) shows the case that nitrogen molecules in the ground and the excited states approach the on-top site of the Zn (Se) atom in $ZnSe_2H_6$ ($SeZn_2H_6$) with the nitrogen bond parallel to

the surface of ZnSe layers (side-on) and with the bond perpendicular to the Se-Zn-Se (Zn-Se-Zn) plane of the cluster. In these models, the bond length between the Zn and the Se atoms of the clusters in Fig. 1 is fixed at 3.995 Å [6]. The length of Zn-H and Se-H are fixed at 1.59, 1.46 Å, respectively [7].
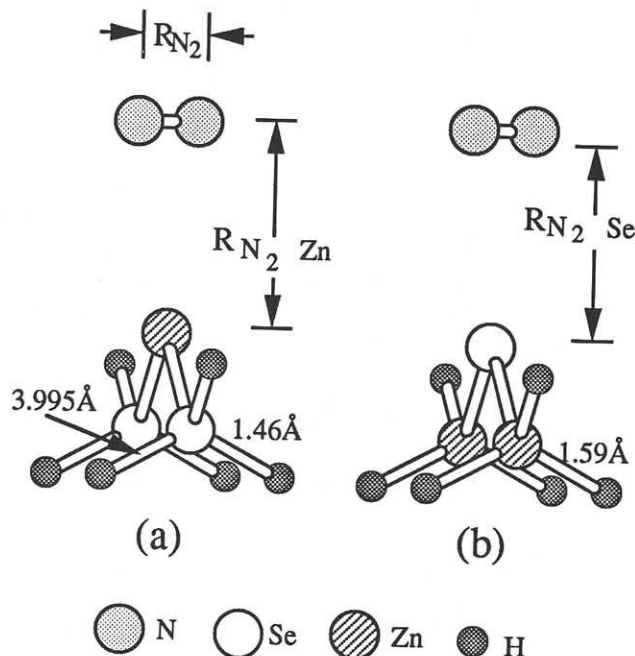

Fig. 1 The cluster models for the calculations of electronic states composed of (a) $N_2 - ZnSe_2H_6$ and (b) $N_2 - SeZn_2H_6$. The nitrogen molecules are put on the side-on, on-top site of central Zn and Se atoms of the clusters, respectively.

The calculations were performed with valence double zeta basis sets except hydrogen. For hydrogen, a single zeta basis set was used. The nitrogen and hydrogen basis sets were (7s4p)/[3s2p] and (4s)/[1s] from Huzinaga [8] and Dunning Jr. [9], respectively. For Zn and Se, (3s2p5d)/[2s2p2d] and (3s3p)/[2s2p] basis sets and effective core potential (ECP; Ar core) from Hay and Wadt were used, respectively [10]. The total energy of the clusters with the nitrogen in the ground (RHF) and the excited (ROHF) states were calculated at the SCF (Hartree-Fock) level [11]. The calculations were carried out with the program HONDO version 7.0 [12].

A free nitrogen molecule has two kinds of degenerated orbitals π_u and π_g. Since the cluster models adopted here have C_{2v} symmetry, each π_u and π_g orbital is split into two non-degenerate components, respectively. One is parallel and the other is perpendicular to the ZnSe surface. Since the π_g perpendicular component of the nitrogen molecule will form a bonding orbital with the ZnSe surface atom (Zn or Se) when the nitrogen approaches it, the component will be a doubly occupied orbital. Therefore, for the triplet calculation, the π_g and π_u molecular orbitals parallel to the surface are assigned as singly occupied orbitals.

III. Results and Discussion

In Fig. 2, total energy diagrams against the distances R_{N_2-X} (X = Zn or Se) between the center of nitrogen molecule and the Zn atom of the $ZnSe_2H_6$ (or the Se atom of the $SeZn_2H_6$), respectively, are shown. The distances R_{N_2-X} (X = Zn or Se) adopted here are 5.0, 3.0, 2.5, 2.0 and 1.5 Å. The units of the energy and the distance in Fig. 2 are electron-volt and angstrom, respectively. The values above or under the bar in Fig. 2 are the distances of the nitrogen atoms (R_{N-N}) at the most stable point of respective R_{N_2-X} (X = Zn or Se) distances. The equilibrium bond length of nitrogen molecule in the ground state is 1.10 Å [7]. The energy of the $^3\Sigma_u^+$ state of free nitrogen molecule is calculated 6.56 eV (exptl. 6.17 eV [7]) higher than that of the ground state ($^1\Sigma_g^+$).

From the Fig. 2, the nitrogen molecules in the ground state ($^1\Sigma_g^+$) and in the excited state ($^3\Sigma_u^+$) do not approach the Se atom of $SeZn_2H_6$ and do not begin to dissociate on it energetically. Neither does the nitrogen molecule in the ground state to the Zn atom of $ZnSe_2H_6$. On the other hand, as the nitrogen molecule in the triplet state approaches the Zn atom of the $ZnSe_2H_6$, the nitrogen becomes stable and the bond length becomes longer than 1.29 Å, which is the equi-
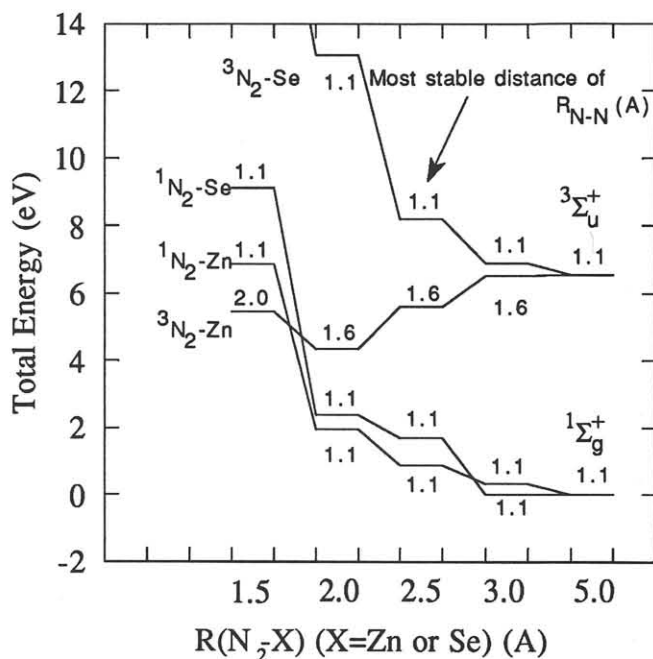

Fig. 2 The total energy diagram of the clusters $N_2 - ZnSe_2H_6$ and $N_2 - SeZn_2H_6$ against the distances $R_{N_2} - X$ (X = Zn or Se) between the center of nitrogen molecule and the central atom (Zn or Se) of the clusters. The values above or under the bar are the distances of the nitrogen atoms (R_{N-N}) at the most stable point of respective R_{N_2-X} (X = Zn or Se). The units of energy and distance are electron-volt and angstrom, respectively.

librium distance of the triplet nitrogen bond [7]. These results indicate that only the lowest excited triplet $^3\Sigma_u^+$ nitrogen molecule can be dissociated on a Zn atom of ZnSe (100) surface. Note that the cluster models adopted here cannot completely describe the dissociation reaction of nitrogen molecule on the ZnSe (100) surface because of ignorance of the surface neighbor Zn atoms with the cluster model. However, since the shortest distance between the Zn atoms of the reconstructed ZnSe (100) surface is 2.47 Å [13], the adsorbed nitrogen bond length of 1.6 Å in our models is thought to be a symptom of the dissociation and the incorporation of a nitrogen atom into the Se site. When the bond length of the nitrogen molecule on the Zn atom becomes 2.0 Å, the total energy slightly increases and a barrier for dissociation appears in Fig. 2. However, the energy is still 2.37 eV lower than that of the case with $R_{^3N_2-Zn} = \infty$. For more detailed discussion on the mechanism of the nitrogen dissociation and incorporation, larger cluster model is required. The larger cluster model will show the dissociation and the incorporation of the nitrogen without the barrier.

For dissociation of a singlet nitrogen molecule on ZnSe surface, it needs larger energy than that of a triplet state molecule, because a singlet molecule has a
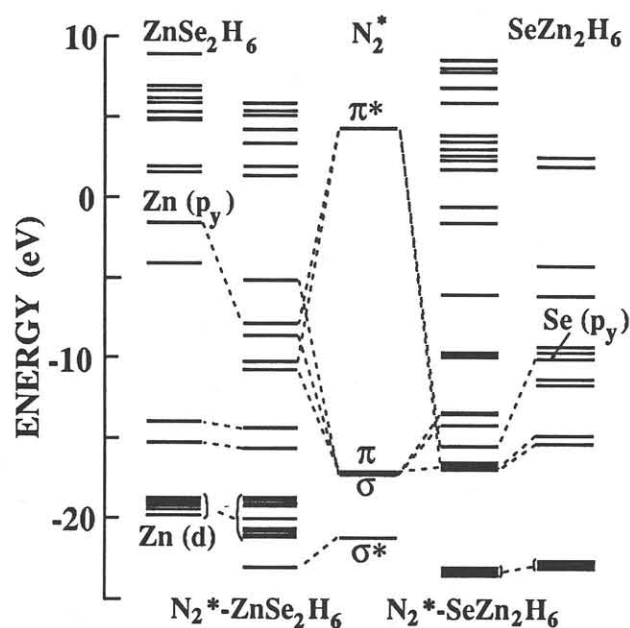
337

Fig. 3 The orbital correlations between nitrogen molecule and ZnSe cluster models.

triple bond against a double bond of a triplet molecule.

Let us discuss the mechanism of the dissociation of the triplet nitrogen molecule. In this case, Zn valence p orbital perpendicular to the Se-Zn-Se plane in $ZnSe_2H_6$ and nitrogen π_g antibonding orbital play important roles. When the triplet nitrogen molecule approaches the Zn atom of the $ZnSe_2H_6$, the overlap integrals between π_g antibonding orbital and Zn valence p orbital perpendicular to the Se-Zn-Se plane increases and the bond distance of nitrogen molecule becomes longer. When the triplet nitrogen molecule approaches the Se atom of the $SeZn_2H_6$, the spatial overlap integrals between π_g antibonding and the Se valence p orbital also increases. However, since the orbital energy-gap (14.15 eV) between the Se valence p localized orbital and the nitrogen π_g antibonding orbital is larger than that (5.71 eV) between the Zn valence p localized orbital and the nitrogen π_g antibonding orbital, as shown in Fig. 3, the nitrogen on the Se cannot obtain enough stabilization energy compared with the nitrogen on the Zn atom. A large energy-gap between two molecular orbitals makes their interaction weak. Then nitrogen molecule on the Se does not become stable energetically. Zinc d orbitals have small contribution for the nitrogen dissociation in our models.

IV. Summary

Nitrogen molecular adsorption and dissociation on ZnSe (100) surface has been studied by ab initio molecular orbital theory. Based on the electronic structure and energetics, the excited ($^3\Sigma_u^+$) nitrogen molecule can be selectively adsorbed and dissociated on a Zn atom of the ZnSe surface.

References

1. K. Ohkawa, T. Karasawa and T. Mitsuyu, J. Cryst. Growth, 111, 797 (1991).

2. M. A. Haase, J. Qiu, J. M. DePuydt and H. Cheng, Appl. Phys. Lett., 59, 1272 (1991).

3. H. Jeon, J. Ding, W. Patterson, A.V. Nurmikko, W. Xie, D.C. Grillo, M. Kobayashi and R.L. Gunshor, Appl. Phys. Lett., 59, 3619 (1991).

4. S. Hayashi, A. Tsujimura, S. Yoshii, K. Ohkawa and T. Mitsuyu, to be submitted.

5. F. Kitagawa, T. Mishima and K. Takahashi, J. Electrochem. Soc., 127, 937 (1980).

6. H. P. Singh and B. Dayal, Phys. Stat. Sol., 23, K93 (1967).

7. G. Herzberg, Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules (D. van Nostrand Co.,Inc., Princeton, 1950).

8. S. Huzinaga, gaussian basis sets for molecular calculations (elsevier, Amsterdam, 1984).

9. T. H. Dunning Jr., J. Chem. Phys., 53, 2823 (1970).

10. P. J. Hay and W. P. Wadt, J. Chem. Phys., 82, 270 (1985).

11. C. C. J. Roothaan, Rev. Mod. Phys., 23, 69 (1951); 32, 179 (1960).

12. M. Dupuis, J. D. Watts, H. O. Villar and G. J. B. Hurst, HONDO version 7.0, Quantum Chemistry Program Exchange #544 (1987).

13. P. H. Fuoss, D. W. Kisker, G. Renaud, K. L. Tokuda, S. Brennan and J. L. Kahn, Phys. Rev. Lett., 63, 2389 (1989).