

Stability and Mobility of Surface Precursors for Reaction Gases in W-CVD

Ryotaro IRIE, Nobuyoshi KOBAYASHI,
Jiro USHIO, Yoshiaki TAKEMURA, and Takuya MARUIZUMI

Hitachi, Ltd. Central Research Laboratory
1-280, Higashi-koigakubo, Kokubunji-shi, Tokyo 185, Japan
Fax: +81-423-27-7748, Tel: +81-423-23-1111 (ext. 3121)

This work theoretically analyzes surface species in selective W-CVD using WF₆ and SiH₄. We investigated surface species on W surface models (W9 or W25) with an approximate molecular orbital method (LEAF). According to our calculations, both of the dominant surface species (predicted as SiF₃ and H) are mobile on the W surface, and the collision between SiF₃ and H could lead to SiHF₃ gas formation. This picture suggests the origin of the main gaseous product (SiHF₃) observed by infrared spectroscopy.

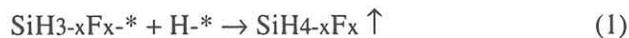
1. INTRODUCTION

For designing and controlling CVD processes, it is very important to reveal the elementary processes (gas-phase reactions, adsorptions, surface migrations, etc.). In this work, we theoretically analyze the surface reactions of selective W-CVD using WF₆ and SiH₄, which has been proven a promising technique for integrated circuit metallization. Experimentally, infrared-spectroscopic study of the reaction gases showed that this W-CVD process has SiHF₃, SiF₄, and H₂ as gaseous products. Moreover, most of the SiH₄ is converted to SiHF₃¹⁾. On the other hand, mass-spectroscopic study suggested that SiF₄ could be a reaction product²⁾. This characteristic product composition must be a reflection of the reaction mechanism for this process. Theoretical analysis is indispensable to get a further understanding of mechanism.

2. APPROACH

In this work, we focus on the processes related to fluorosilanes' evolution from the growing surface in selective W-CVD. In the analysis of the fluorosilanes' formation, we take the following assumptions.

(i) All fluorosilanes are generated from the growing W surface by the reverse reactions of dissociative adsorptions:



and



where * denotes any site on the surface.

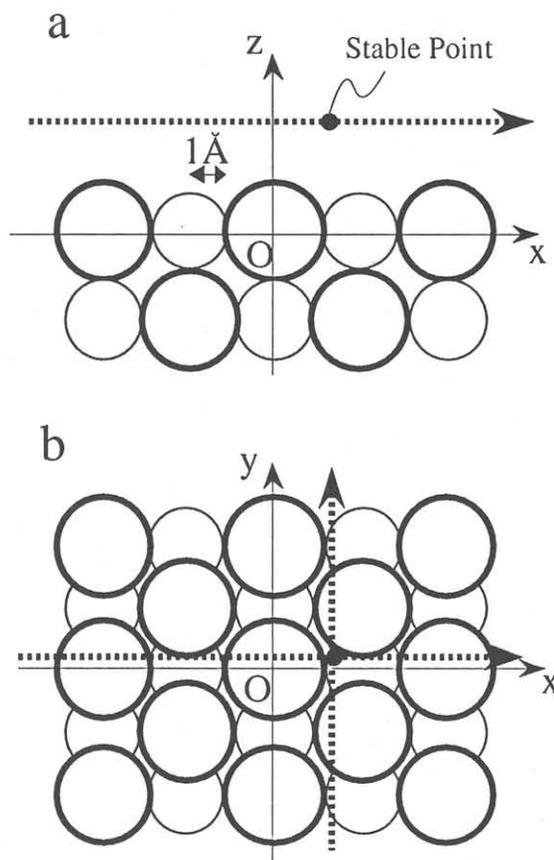


Fig. 1 W (110) surface model (W25) employed for surface migration analyses.
a: Side view. b: Top view. Open circles: W atoms. X-Y plane: the surface. Broken lines: Assumed migration paths.

(ii) The surface precursors always touch the bare (110) surface of W bcc crystal (the direction of the surface is based on XRD analyses³⁾).

In order to investigate the mobility of precursors, a W25 cluster is employed as the surface model, the area of which is a few times larger than the surface model used for the stability analyses of the precursors⁴⁾. Fig. 1 shows side and top views of the W25 cluster with a Cartesian coordinate system. In Fig. 1, each open circle is a W atom, and the first-layer atoms are located at the X-Y plane (Z=0).

The optimized atomic configuration of each adsorption species is evaluated by minimizing the potential energy with the steepest descent method, while the positions of native surface atoms are fixed throughout optimization. The potential energy, or total energy of each adsorption system in an atomic configuration is calculated by an approximate molecular orbital method, LEAF^{5,6)}. In the LEAF method, one-electron wavefunctions (molecular orbitals) are calculated by solving the eigen-value problem of the one-electron Hamiltonian, the potential part of which is the 'linkage of embedded atomic fields'⁵⁾. Under this potential, an electron, which can take a position everywhere in the system in a certain probability, always feel the neutral-state potential of the nearest atom, exclusively. From the molecular orbitals, one can calculate the total energy of the system by the equation:

$$E_T = \sum_i v_i \varepsilon_i + \sum_{\alpha} \alpha (1/2) Q_{\alpha} (Q_{\alpha}-1) \gamma_{\alpha} + \sum_{\alpha < \beta} F_{\alpha\beta} (Q_{\alpha}, Q_{\beta}, R_{\alpha\beta}) + \text{const.}, \quad (3)$$

where v_i denotes the electron occupation number in the i -th molecular orbital, ε_i the energy of the i -th molecular orbital, Q_{α} the electric charge of the α -th atom (evaluated by the Mulliken analysis of the above molecular orbitals), γ_{α} the inter-electronic repulsion energy in the α -th atom, and $F_{\alpha\beta}$ the inter-atomic electrostatic energy as a function of Q_{α} , Q_{β} , and $R_{\alpha\beta}$ (inter-atomic distance)⁶⁾. The feasibility of this molecular orbital method was checked previously⁴⁾.

3. RESULTS AND DISCUSSION

According to our calculations of surface precursor stability (Fig. 2), SiF3 radicals and H atoms could be dominant species on the growing W surface⁴⁾.

However, the formation of fluorosilanes requires the mobility of the precursors on the surface as well as the stability. In order to investigate the mobility of surface precursors, we evaluated the stable positions (or optimized structures) of several adsorbates (H, F, Si, Cl, and SiH3) on the relatively large surface model (W25). According to the optimization results, H and Si atoms have stable positions at hollow sites, while F, Cl, and SiH3 adsorbates are favorably located at on-top sites. Concerning with the H and Si positions on W (110) surface, our results are consistent with the related experiments^{7,8)}.

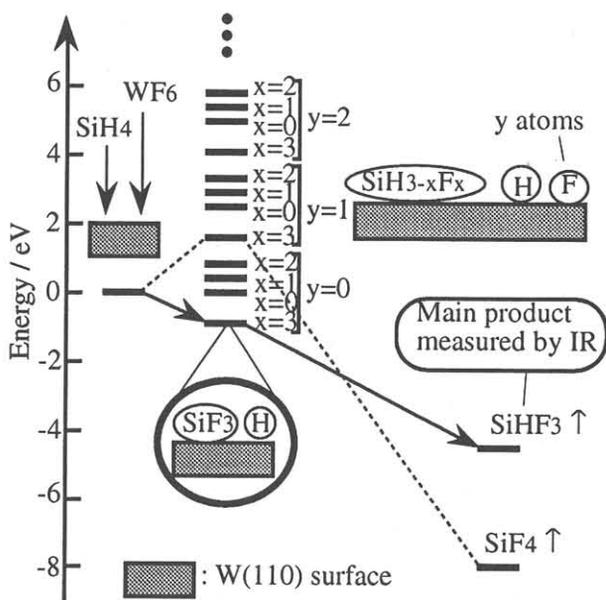


Fig. 2 Calculated energy levels of surface precursors for fluorosilane formation on the growing surface in W-CVD.

If adsorbates on the surface have an appropriate amount of kinetic energy, they could move around their stable positions and hop from one stable position to another one in the neighborhood. Surface migration of adsorbates can be defined as the sequence of hops between stable positions. Thus, in order to assess the degree of mobility of an adsorbate, we calculated the potential energy variation when the adsorbate moves along the straight migration paths, which include the stable point and are parallel to the X or Y direction (see Fig. 1).

The calculation results for Si and SiH3 adsorbates are shown in Figs. 3-4. We estimated the activation energies for two surface migration paths (E_{ax} and E_{ay}) by measuring the height of the barrier in the immediate neighborhoods of the stable points (filled circles). The representative activation energies (E_a) should be the smaller of E_{ax} and E_{ay} . Striking difference in E_a 's between Si and SiH3 was found (2.3 eV and 0.2 eV, respectively). We also estimated the E_a 's for H, F, and Cl to be 0.2 eV, 0.5 eV, and 0.2 eV respectively. In addition, the estimated E_a for H agrees with the experimental value⁷⁾. These results suggest that adsorbates with a single unpaired electron (i.e., monovalent adsorbates such as SiH3, H, F, etc.) migrate on the metal surface easily.

Thus one can expect that both of the dominant species (predicted to be SiF3 and H) are mobile on the growing W surface, and the collision between SiF3 and H could lead to the formation of SiHF3 gas. This picture suggests the origin of the main gaseous product (SiHF3) observed by the infrared spectroscopy¹⁾.

4. CONCLUSIONS

We calculated the stability and the mobility of surface precursors in selective W-CVD with an approximate molecular orbital method (LEAF). According to our calculations, SiF₃ radicals and H atoms could be dominant species on the W surface. Besides, the estimated activation energies for surface migration of monovalent species (F, Cl, silyl, etc.) are as small as that of the mobile H atom. Thus both of the dominant species (SiF₃ and H) are mobile on the W surface, and the collision between SiF₃ and H could lead to the formation of SiHF₃ gas. This work revealed an atomistic picture of the formation of the main gaseous product, which is observed by infrared spectroscopy, and shows that our theoretical approach is effective in analyzing CVD surface processes.

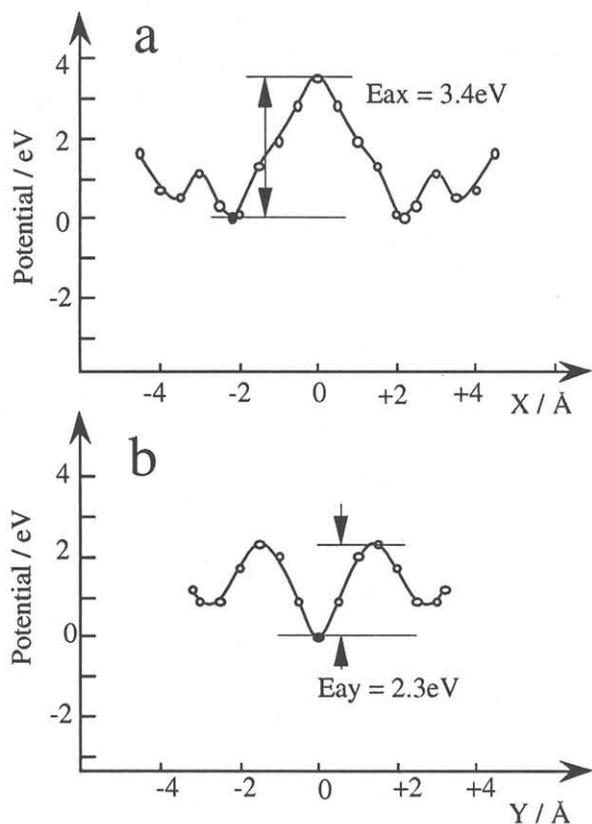


Fig. 3 Potential energies along Si migration paths on W(110) surface model (W25)
 a. In the X direction. Cartesian coordinate of Si adsorbate: (X, 0.00, 2.19) in angstrom.
 b. In the Y direction. Cartesian coordinate of Si adsorbate: (2.21, Y, 2.19) in angstrom.

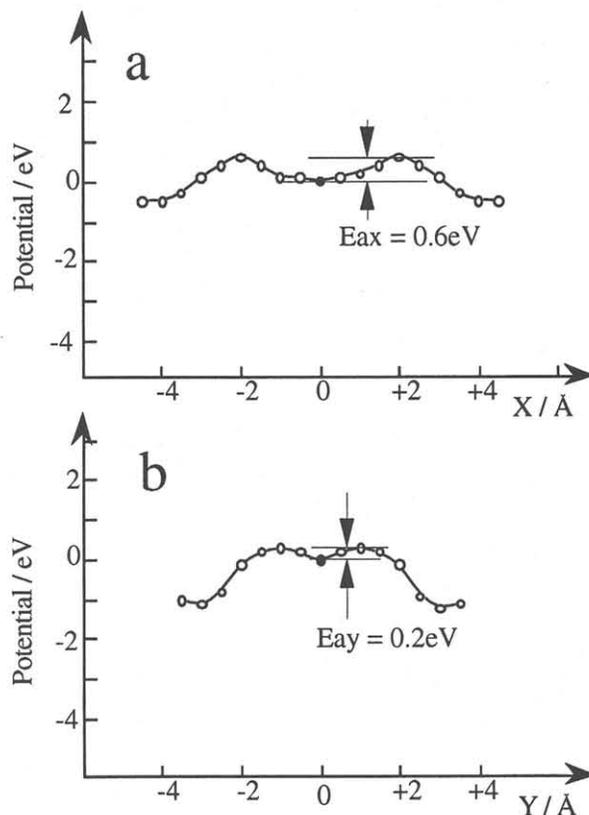


Fig. 4 Potential energies along SiH₃ migration paths on W(110) surface model (W25)
 a. In the X direction. Cartesian coordinate of Si atom in SiH₃: (X, 0.00, 3.25) in angstrom.
 b. In the Y direction. Cartesian coordinate of Si atom in SiH₃: (0.00, Y, 3.25) in angstrom.

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