Dissociative Adsorption Mechanism of Product Gas in W-CVD Revealed by Molecular Orbital Calculation and Its Determinant Role in Filling Features

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Extensive Molecular Orbital (MO) calculation revealed that dissociative adsorption of SiHF₃ to SiF₃ and H at active surface sites is the substantial mechanism in surface-site-blocking model, which is implied by the growth rate reduction in W-CVD (Chemical Vapor Deposition) when product gas SiHF₃ is added to the source gases WF₆ and SiH₄. Film profile calculation with the model derived from MO calculation showed that dissociative adsorption of SiHF₃ plays determinant role in filling micro scale features.

1. Introduction

It is well known that W-CVD using WF₆ and SiH₄ give rather poor step coverage in filling contact holes and trenches¹). This fact has been explained as reverse reaction in feature, but the reverse reaction rate was used in the framework of fitting parameter²). Recently, other experiment showed that addition of product gas SiHF₃ to source gases reduces film growth rate, and surface-site-blocking¹) model was proposed in which adsorbed SiHF₃ blocks surface sites otherwise used for deposition reaction. Although this model is expected to relate poor step coverage with SiHF₃ in micro scale features, no molecular picture of adsorption, the substantial mechanism in this model, has been proposed from the consideration based on theoretical analysis.

In this work, we carried out MO calculation in order to make clear this molecular picture of adsorption, in other words, dissociative adsorption of SiHF₃. And we also performed film profile calculation in micro scale features with the model derived from the calculation above in order to obtain characteristics of this CVD process.

2. Dissociative Adsorption Mechanism of SiHF3 Analyzed by MO calculation

We used *ab initio* MO program HONDO7 which can give molecular adsorption energy with chemical accuracy. Summary of calculation is shown in Table 1. Tungsten surfaces were modeled by W clusters, which correspond to step or kink, important sites for film deposition reactions.

The dissociative adsorption mechanism obtained is shown in Fig. 1. Total dissociation process is thought to be composed of two elementary dissociation steps, with in each step one chemical species dissociates into two sub-species. Although dissociative adsorption on terrace is not energetically favorable³, out results show that it can occur at step and/or kink.

Considering the stability of adsorption states in energy and stoichiometry for adsorbates, only the two reaction paths are possible. The first path (dotted line in Fig.1) consists of two steps. The product gas SiHF₃ first dissociatively adsorbs on the surface to give two adsorbates, SiHF₂ and F(adsorption state A). One of the adsorbate SiHF₂ then dissociates into SiHF and F (state D). The second path (solid line in Fig.1)

is the dissociative adsorption of SiHF₃ into two adsorbates, SiF₃ and H (state B). Though state D is energetically most stable, it is derived only from the state A which is less stable than B. We think the second path is major reaction and this two-site-blocking process is substantial mechanism in surface-site-blocking model in W-CVD.

3. Role of SiHF₃ Dissociative Adsorption in Filling Features

We have developed 2D-film profile simulator based on Ballistic Transport and Reaction Model (BTRM)⁴) and we improved the model so that the redistribution and readsorption of product gas can be incorporated. We used two types of rate equations. One is in accordance with two-siteblocking model derived from MO calculation and the other is first-order rate equation of source gas SiH₄ (conventional model). Each rate equation is shown as follows:

$$R = \frac{k_1 P_{SiH4}}{1 + k_2 \sqrt{P_{SiHF3}}}$$
(1)

$$R = k_1 P_{SiH_4} \tag{2}$$

The calculated profiles are shown in Fig.2. Film profile with our model shows much poor coverage than with conventional model to give good agreement with experimental result.

The calculated equilibrium flux distribution of gases in trench are shown in Fig.3. Although the flux of source gases, WF_6 and SiH₄, decrease along the side wall from top to bottom because of the gas consumption during deposition reaction, the change is very little and the flux difference between the two models is less than one percent. This means the sticking coefficients of the sources gases are very small in this CVD condition.

On the other hand, the flux of product gases, SiHF₃ and H_2 , largely increases as the vertical position becomes lower because the gases are mainly emitted from walls and bottom, and the flux with our model is 10 - 20 % smaller than with conventional model. This result shows that with out model, the SiHF₃ within the trench reduces the growth rate because of the dissociative adsorption, and thus reduced the amount

of product gases during the deposition reaction to give poor step coverage.

4. Conclusion

With extensive MO calculation, we revealed that substantial mechanism in surface-site-blocking model in SiH₄ reduced W-CVD, corresponds to dissociative adsorption of product gas SiHF₃ to SiF₃ and H at active surface sites. Along with MO calculation, film profile prediction and gas flux distribution derived from it made us to conclude that characteristics of this W-CVD should be attributed to dissociative adsorption of product gas rather than previously reported reverse reaction.

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References

- C.A.van der Jeugd et al., Advanced Metallization for ULSI Applications in 1993, p369 (Conf. Proc. ULSI-IX, 1994, Materials Research Society)
- (2)T.S.Cale et al., Advanced Metallization for ULSI Applications, p101(Conf. Proc. ULSI-VII, 1992, Materials Research Society)
- (3) R.Irie et al., Advanced Metallization for ULSI Applications in 1993, p435 (Conf. Proc. ULSI-IX, 1994, Materials Research Society)
- (4) T.S.Cale and G.B.Raupp, J.Vac.Sci.Technol. **B8**, 1242(1990)

Table 1 Summary of MO calculations for dissociative adsorption of $SiHF_3$. Plausible adsorbates and their optimized structures are tabulated.

W and W₂ designate on-top site and bridge-site at tungsten surface, respectively.

Adsorbate	Н	F	SiHF ₂	SiF ₃	SiHF	SiF ₂
Adsorbate Position from surface in Å	H 1.74 W	F 1.96 W	SiHF ₂ 2.60 W	SiF ₃ 2.58 [*] W	SiHF 2.08 [*] W ₂	SiF ₂ 2.05 [*] W ₂
MO level	Hartree-Fock self consistent field (SCF)				Multi Configuration SCF	
Basis set	MIDI-4 for Si, H, O and relativistic effective core potential for W					

* corresponds to the height of Si position from surface.



Fig. 1 Dissociative adsorption mechanism of product gas SiHF₃ in W-CVD ascertained by MO theory. Major adsorption path leads to two-site-blockage by SiF₃ and H.



Fig. 2 Effect of dissociative adsorption of product gas SiHF3 on film profile in W-CVD.

(a) With rate equation in proportional to SiH₄ pressure (conventional model)

(b) With rate equation based on two-site-blocking reaction scheme revealed in this study. Growth rate R is formulated as

$$R = k_1 P Si H_4 / [1 + k_2 (P Si HF_3)^{1/2}]$$

(c) Experimentally observed film profile obtained at process condition:

 $PSiH_4 = 25$ mTorr, $PWF_6 = 45$ mTorr, and Temperature = 350 °C. (ref.1)



Fig. 3 Equilibrium flux distribution along side wall witnin trench in W-CVD .

(a) Source gases: WF 6 and SiH4

(b) Product gases: SiHF 3 and H2