# Identification of different gas-phase reaction modes of WF<sub>6</sub> with SiH<sub>4</sub> for deposition of WSi<sub>n</sub> films: powder formation and WSi<sub>n</sub> cluster synthesis

Naoya Okada, Noriyuki Uchida, Shinichi Ogawa, and Toshihiko Kanayama

National Institute of Advanced Industrial Science and Technology (AIST)

1-1-1, Umezono, Tsukuba, Ibaraki, 305-8568, Japan Phone: +81-29-861-2512 E-mail: okada-naoya@aist.go.jp

#### Abstract

We elucidate the comprehensive mechanism of gasphase reactions of WF<sub>6</sub> with SiH<sub>4</sub> for formation of WSi<sub>n</sub>  $(0 < n \le 12)$  films. Three gas-phase reaction modes are clearly identified depending on the partial pressure ratio of SiH<sub>4</sub> to WF<sub>6</sub>: (1) powder formation, (2) Fluorine reduction, and (3) W-atom-encapsulated Si<sub>n</sub> cage clusters synthesis modes. These findings enable us to precisely control the deposited film properties with definite Si and F contents while inhibiting the powder formation.

## 1. Introduction

For decades, W and W silicides (WSi<sub>n</sub>) have been used as electrode materials in Si LSIs because of their low resistivity and high reliability. It is well known in the CVD of these films using SiH<sub>4</sub> and WF<sub>6</sub> source gases that the reaction mechanism drastically changes from a surface reaction to a gas-phase reaction at a partial pressure ratio of SiH<sub>4</sub> to WF<sub>6</sub> ( $PR_{SiH4/WF6}$ ) = ~1.<sup>[1]</sup> Accordingly, deposition rates and film properties distinctively vary. Although the gas-phase reaction leads to a high deposition rate, this mode has a concern about powder generation.<sup>[1]</sup> By the use of the gas-phase reaction, Saito *et al.* showed that the Si content of WSi<sub>n</sub> films can be increased to  $n < \sim 3$ .<sup>[2, 3]</sup> However, what modes are present in the gas phase reactions remain to be elucidated.

In contrast, we demonstrated the formation of WSi<sub>n</sub> films with much higher Si contents, up to  $n \le 12$  by preforming Watom-encapsulated Si<sub>n</sub> cage clusters in the gas phase: *i.e.*, the cluster-preforming deposition (CPD) method.<sup>[4]</sup> The WSi<sub>n</sub> (n = 12) film exhibits particularly useful properties as a contact material for source/drain in Si CMOS: a reduction of the electron Schottky barrier height to 0.32 eV at W/WSi<sub>n</sub>/n-type Si, excellent barrier properties against Cu diffusion, and an excellent contact hole coverage.<sup>[5]</sup> A question remains as to why the CPD is free from the power formation.

In this work, we identify that the three different modes are present in the gas-phase reactions of SiH<sub>4</sub> and WF<sub>6</sub>; *i.e.*, powder formation mode, Fluorine (F) reduction mode, and W-atom-encapsulated Si<sub>n</sub> ( $n \ge 6$ ) cage cluster synthesis mode.

## 2. Experimental

The WSi<sub>n</sub> film was prepared using SiH<sub>4</sub> and WF<sub>6</sub> on a SiO<sub>2</sub>/Si substrate by a cold wall CVD (FIG. 1 (a)) or a hotwall CPD system (FIG. 1 (b)). The number density of powders formed the film,  $N_P$  was estimated from dark field images of optical microscope (OM) and scanning electron microscope (SEM) images over an area of ~1 mm<sup>2</sup>. The substrate stage temperature  $T_S$  was set to 260–400 °C. SiH<sub>4</sub> and WF<sub>6</sub> were introduced into the reactor at a mass flow rate of 0.2–1 SCCM and 0.01–0.2 SCCM, respectively, and the gas pressure was maintained at a total pressure  $P_{\rm T}$  of 10 Pa (TABLE 1). For CPD, hydrogenated W-atom-encapsulated WSi<sub>n</sub>H<sub>x</sub> ( $n \le 12$ ) clusters are preformed by reaction of WF<sub>6</sub> and SiH<sub>4</sub> in the gas phase and then deposited onto a substrate. On the substrate surface heated at  $T_{\rm S} = 350-400$  °C, WSi<sub>n</sub>H<sub>x</sub> clusters are thermally dehydrogenated and coalesce to the WSi<sub>n</sub> film with less hydrogen content.<sup>[4]</sup>

## 2. Powder formation mode in CVD

As  $PR_{SiH4/WF6}$  increased > 1, the *n* value of the WSi<sub>n</sub> film drastically increased (FIG. 2).<sup>[1]</sup> This indicates the reaction mechanism of SiH<sub>4</sub> and WF<sub>6</sub> changes from the surface reaction to the gas-phase reaction. Accordingly, the film morphology also changed (FIG. 3 (a) and (b)), and N<sub>P</sub> peaked near the onset of gas-phase reaction (FIG. 4). This behavior indicates that the powder generation is due to the high reactivity of  $WF_6$ with SiH<sub>4</sub> in the gas phase. In fact, the reaction of WF<sub>6</sub> and SiH<sub>4</sub> starts at a low temperature ~120 °C. Once a WF<sub>6</sub> molecule is reduced by a SiH<sub>4</sub> with HF detachment to an even more reactive WF<sub>5</sub>, it collides with another SiH<sub>4</sub> to produce an adduct  $WF_{v}(SiH_{x})_{n}$  ( $y \le 5, n < 6$ ). These adduct clusters are highly reactive with each other, enabling the rapid polymerization reaction accompanied with HF desorption if they are allowed to collide with other clusters or WF6 molecules. This polymerization reaction continues as far as the product cluster contains F, resulting in the formation of powders by chain reactions among these reactive clusters.

## 3. Fluorine reduction mode in CVD

When  $PR_{\text{SiH4/WF6}}$  exceeded ~100, the film morphology did not change (FIG. 3 (b) and (c)) but  $N_P$  decreased gradually with increasing  $PR_{\text{SiH4/WF6}}$ . This is because the collision frequency between the WF<sub>y</sub>(SiH<sub>x</sub>)<sub>n</sub> clusters and SiH<sub>4</sub> increases with  $PR_{\text{SiH4/WF6}}$ ; consequently, the clusters lose the F content y with the increase of n, resulting in the lower reactivity of the product clusters. Furthermore, the reactivity drops drastically when  $n \ge 6$  and y = 0: WSi<sub>n</sub>H<sub>x</sub> ( $n \ge 6$ ) clusters. In fact, the WSi<sub>n</sub> film does not reach n = 6 even when  $PR_{\text{SiH4/WF6}} >$ ~1000.

## 4. WSi<sub>n</sub>H<sub>x</sub> ( $n \ge 6$ ) cluster synthesis mode in CPD

Under the CPD condition of an extremely high  $PR_{\text{SiH4/WF6}}$ , sufficient times of collisions between the WF<sub>y</sub>(SiH<sub>x</sub>)<sub>n</sub> cluster and SiH<sub>4</sub> molecules are provided. The resulting film is in an amorphous state (FIG. 3 (d)), which is densely packed with clusters without vacancy and void (FIG. 5), with very few residual F of < ~0.1 at. % (FIG. 6) because of the sufficient reduction reaction with SiH<sub>4</sub> in the gas phase. This value is much lower than that in a conventional CVD film of > ~1 at. %. The *n* value of the clusters was determined by the gas temperature (FIG. 7), indicating that the energy barrier for reaction between the  $WSi_nH_x$  cluster and  $SiH_4$  increases with *n*. Therefore, the reaction probability is very low when  $WSi_nH_x$  $(n \ge 6)$  clusters collide each other in the gas phase, resulting in the almost complete inhibition of the powder generation. This suppression becomes more when n is saturated near 12 because  $WSi_{12}H_x$  cluster is the most stable final product.

## 5. Conclusions

We demonstrated the presence of three reaction modes in the gas phase of SiH<sub>4</sub> and WF<sub>6</sub> well-separated as a function of PR<sub>SiH4/WF6</sub>.

1. Near the onset of the gas-phase reaction turning from the surface reaction, the product species contains appreciable F amounts and "Powder formation mode" dominates.

TABLE 1. Deposition conditions of WSin-CVD

SiH4	WF <sub>6</sub>	PR <sub>SiH4/WF6</sub>	$P_{\mathrm{T}}$	$T_{S}$	Deposition
(SCCM)	(SCCM)		(Pa)	(°C)	time (min)
0.2	0.2	1	10	300	10
0.6	0.2	3	10	300	10
1.0	0.2	5	10	300	10
2.0	0.2	10	10	300	10
5.0	0.05	100	10	300	40
5.0	0.01	500	10	300	60



FIG. 2. Si content of the WSi<sub>n</sub> film and number density of powders N<sub>P</sub> on the substrate after CVD and CPD processes as a function of partial pressure ratio of SiH4 to WF6, PRsiH4/WF6.



FIG. 5 Mass density of the resulting WSin films, estimated by Xray reflectivity analysis, as a function of composition n. The blue curve is the mass density assuming the same atomic density as that of Si, indicating that the film has an atomic density higher than Si.

- 2. Under the condition of  $PR_{SiH4/WF6} > \sim 10$ , the sufficient reaction with SiH4 molecules reduces the F content in the product; i.e., "F reduction mode", where the powder formation is inhibited as PR<sub>SiH4/WF6</sub> increases due to the less reactivity of the product.
- 3. Only under the condition of an extremely high  $PR_{SiH4/WF6}$ , "WSi<sub>n</sub>H<sub>x</sub> ( $n \ge 6$ ) cluster synthesis mode" is available. Our work provides a guideline for the CVD and CPD

WSi<sub>n</sub> films using the gas-phase reactions of WF<sub>6</sub> with SiH<sub>4</sub>.

## References

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FIG. 1. Schematic of (a) cold wall CVD and (b) CPD systems for the WSi<sub>n</sub> film

(a) PR <sub>siHe/WFe</sub> =1	(b) <i>PR</i> <sub>SiH4/WF6</sub> =5
Grain size	Grain size=
~200nm	~50nm
<mark>3 um</mark>	3 um
(c) <i>PR</i> <sub>SiH4/WF6</sub> =100	(d) CPD (n=12.3)
Grain size=	No grain
~50nm	(Amorphous state)
3 um	<u>3 um</u>

FIG. 3. SEM images of the film

morphology prepared by CVD

under (a)  $PR_{SiH4/WF6} = 1$ , (b) 5,

FIG. 4. Dark field OM images (a, b) and SEM images (c, d) of powders on the substrate after (c) 100, and (d) CPD conditions CVD of  $PR_{SiH4/WF6} = 5$  (a, c) and 100 (b, d)

PReside have =

100

b) PREINA DATES

100

500



FIG. 7. Composition ratio n of the WSi<sub>n</sub> film prepared by CPD as a function of the reactor wall temperature. Other conditions were fixed.

FIG. 6. SIMS depth

fluorine (F) in the

profile of the residual

WSi<sub>n</sub> film with n = 12