

Surface and Gas-Phase Reactions in Selective Tungsten CVD as a Function of the SiH_4/WF_6 ratio

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The surface and gas-phase reactions in tungsten chemical vapor deposition (W-CVD) are quantitatively investigated as a function of the inlet gas flow ratio (FR) of SiH_4/WF_6 , using *in-situ* Fourier-transform infrared (FT-IR) spectroscopy. It is clarified that abrupt changes of selectivity and film characteristics at $\text{FR}=1\sim 1.5$ are caused by gas-phase reactions. These gas-phase reactions occur at temperatures as low as room temperature when $\text{FR}>1\sim 1.5$, which are accompanied by visible luminescence.

1. Introduction

Tungsten chemical vapor deposition (W-CVD) using tungsten hexafluoride (WF_6) and monosilane (SiH_4) is the most promising to fill vias and contacts of deep submicron ULSIs. The reaction mechanism, e.g. the transition mechanism between selective and blanket deposition, has recently gathered much attention.

Many workers have reported that both selectivity and film characteristics, such as its composition, resistivity, and stress, strongly depend on the inlet gas flow ratio (FR) of SiH_4/WF_6 as shown in Fig. 1 [1,2,3]. That is, α -W can be selectively deposited on Si and metals without being deposited on silicon dioxide (SiO_2), when $\text{FR}<1\sim 1.5$. On the other hand, selectivity is lost, both Si content and resistivity of the deposited W film greatly increase, and the β -W and WSi_x phases appear in the film, when $\text{FR}>1\sim 1.5$. However, the mechanism of this FR dependence has not been clarified yet.

In this study, the surface and gas-phase reactions are quantitatively investigated using *in-situ* Fourier-transform infrared (FT-IR) spectroscopy. We compare the reactions at room temperature with those at 300°C . As a result, it is newly found that, in the W-CVD at 300°C , the gas-phase reactions are dominant and cause selectivity loss when $\text{FR}>1\sim 1.5$, while the surface reactions are dominant when $\text{FR}<1\sim 1.5$.

2. Experimental

The experimental apparatus consists of the preparation chamber, the cold-wall CVD chamber, and the analysis chamber. In the CVD chamber, the reaction gases were quantitatively analyzed by *in-situ* FT-IR spectroscopy and quadrupole mass spectrometry (Q-mass), as shown in Fig. 2. The inside of the CVD chamber can be observed during W-CVD through a quartz window.

In order to investigate the gas-phase reactions, it is desirable to keep the whole system, the CVD chamber and reaction gases, at the same temperature. Thus, the reactions of SiH_4/WF_6 mixtures were investigated at room temperature. In this experiment, the temperature of the whole system is almost the same as that of the water-cooled CVD chamber wall (20°C). The inlet gas flow ratio (FR) was varied from 0.5 to 25, and the total pressure was 40 Pa (diluted with N_2).

These results were compared with those of the W-CVD at 300°C . The CVD experimental conditions are as follows. The wafer temperature was 300°C . The FR was varied from 0.5 to 3, and the total pressure was 40 Pa (diluted with N_2). Tungsten film was deposited on a 100 nm thick sputter-deposited W film on a thermally oxidized wafer. The wafer was heated from the front side through a quartz window using halogen lamps. The wafer temperature was measured using a Pt-Rh thermocouple. The deposition rate was

measured from the increase in film weight. The partial pressure of the reaction gases is measured from the FT-IR absorbance [4].

3. Results and Discussions

(1) Gas-phase reaction analysis at room temperature

The partial pressure of the reaction gases is shown in Fig. 3. When $FR < 1.3$, the reactions did not occur. When $1.3 < FR < 2.5$, 60~70% of the inlet SiH_4 was consumed to form silicon-tetrafluoride (SiF_4) and trifluorosilane ($SiHF_3$). Other fluorosilanes, such as SiH_3F and SiH_2F_2 , and hydrogen fluoride (HF) were not detected by FT-IR. The Q-mass spectrometry showed that this reaction formed H_2 along with SiF_4 and $SiHF_3$. (H_2 cannot be detected by FT-IR spectroscopy.) Note that visible luminescence was observed around the gas inlet. This implies that the formation of radical species, such as WF_x , SiF_x , was involved in the reactions. When $FR > 2.5$, the reactions continued to form $SiHF_3$ and SiF_4 , although the visible luminescence disappeared.

In those experiments, when $FR > 1.3$, the W powders were deposited onto the CVD chamber wall. The deposit contained β -W, as determined by X-ray Diffraction (XD). The SEM observation of the W powders showed that they consisted of poly-crystalline W.

(2) W-CVD at 300°C

The partial pressure of the reaction gases determined by FT-IR is shown in Fig. 4.

When $FR < 1$, α -W was selectively deposited on W. The by-product gases, $SiHF_3$ and SiF_4 , were formed, and increased with FR . The reaction pathway that forms $SiHF_3$ is considered to be a surface reaction, because of the selective nature of the W deposition. The dependence of the deposition rate on the substrate temperature was investigated. The deposition temperature was varied from 150 to 300°C, and FR was fixed at 0.5. The Arrhenius plot is shown in Fig. 5. The deposition rate is independent of the wafer temperature above 250°C (mass transfer limited), whereas for lower temperatures the deposition rate decreases exponentially with the reciprocal temperature (surface reaction limited). The activation energy for a temperature range of 150~225°C was 0.29 eV. This value almost coincides with the activation energy of 0.28 eV obtained by Rosler [5]. We consider that $SiHF_3$ is formed by the reaction between dissociated hydrogen and SiF_3 on the W surface, and that the formation of $SiHF_3$ or its desorption is the rate limiting step in the surface reaction limited region [4]. The activation energy obtained is considered to correspond to this reaction step.

When $FR = 3$, selectivity was lost, and $SiHF_3$ was mainly formed. The deposited film mainly contained β -W, which is similar to the deposit formed on the CVD wall at room temperature. The amount of $SiHF_3$ formed at room temperature was no less than half of that formed at 300°C. Considering these results, it is concluded that the gas-phase reactions are dominant in the W-CVD at 300°C.

4. Conclusion

It is clarified that the abrupt changes of both selectivity and film characteristics are caused by the gas-phase reactions of SiH_4/WF_6 mixtures when $FR > 1.3$. These gas-phase reactions occurred at temperatures as low as room temperature, and were accompanied by visible luminescence. When $FR < 1.3$, α -W was selectively deposited by the surface reactions that mainly form $SiHF_3$. It is postulated that silicon subfluorides (mainly SiF_3) and dissociated hydrogen react and form $SiHF_3$ on the W surface, and that the activation energy for $SiHF_3$ formation or desorption is 0.29 eV.

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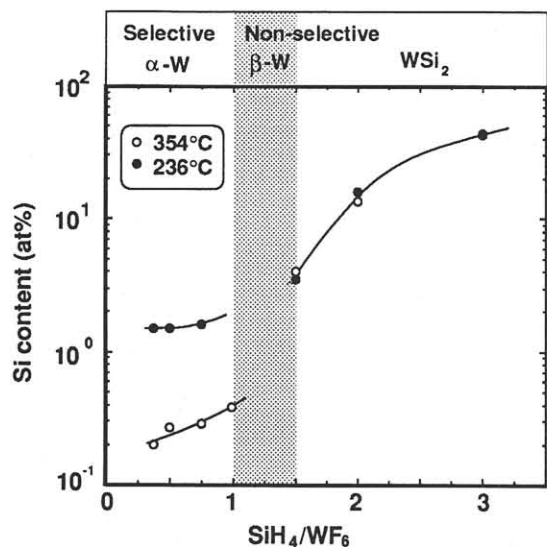


Fig. 1 Dependence of Si content, selectivity, and film composition of W film on SiH_4/WF_6 : $\text{SiH}_4=30\text{-}130$ sccm, $\text{WF}_6=80$ sccm, total=1300 sccm, total pressure=85 Pa

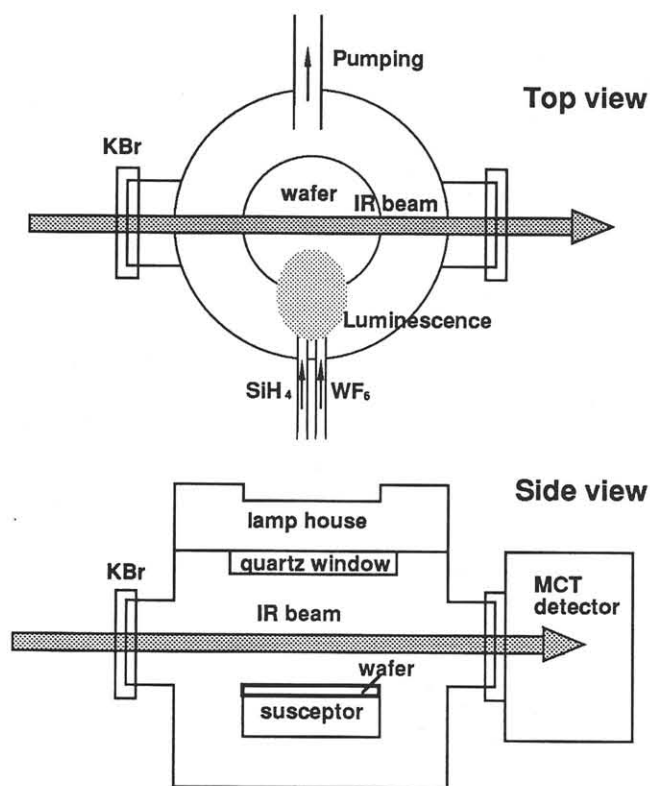


Fig. 2 Schematic diagram of CVD chamber

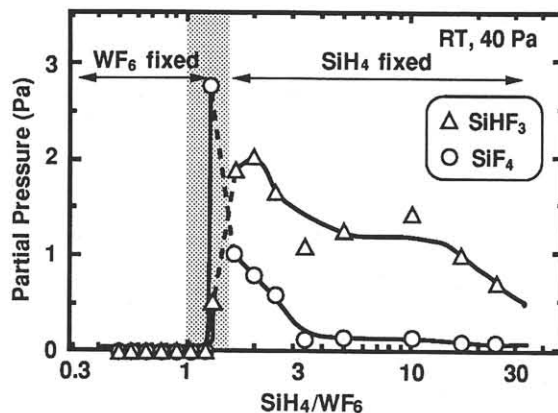


Fig. 3 Dependence of partial pressure of reaction product gases on SiH_4/WF_6 :
(i) $\text{SiH}_4=25\text{-}65$ sccm, $\text{WF}_6=50$ sccm, $\text{N}_2=425$ sccm
(ii) $\text{SiH}_4=50$ sccm, $\text{WF}_6=2\text{-}30$ sccm, $\text{N}_2=425$ sccm

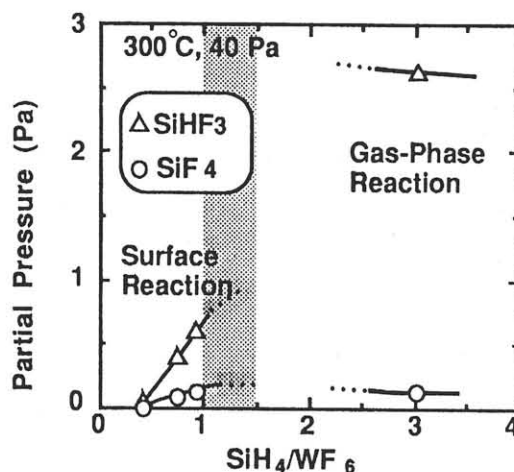


Fig. 4 Dependence of partial pressure of reaction product gases on SiH_4/WF_6 : $\text{SiH}_4=8\text{-}60$ sccm, $\text{WF}_6=20$ sccm, $\text{N}_2=500$ sccm

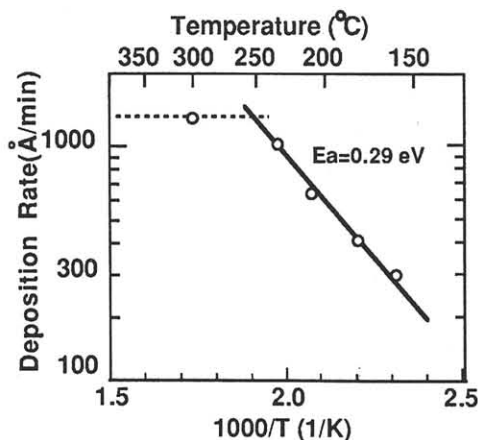


Fig. 5 Arrhenius plot of W deposition rate vs. reciprocal temperature: $\text{SiH}_4=25$ sccm, $\text{WF}_6=50$ sccm, $\text{N}_2=425$ sccm, total pressure=40 Pa