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In-situ Infrared Spectroscopy of Selective CVD of Tungsten Using WF₆ and SiH₄

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The selective chemical vapor deposition (CVD) of tungsten (W) is investigated using *in-situ* infrared (IR) spectroscopy and Auger electron spectroscopy. The IR spectra of reaction gases show that trifluorosilane (SiHF₃), not silicon tetrafluoride (SiF₄), is the main by-product species. The chemical reaction of selective W-CVD is expressed as WF₆ + $2SiH_4 \rightarrow W + 2SiHF_3 + 3H_2$. The reaction pathway for SiHF₃ formation is thought to be the surface reaction of dissociated H with SiF₃ on the W surface. In this reaction, SiF₃ is produced by the surface reaction of WF₆ with solid Si, which is formed by the SiH₄ dissociation on the W surface.

1. Introduction

Chemical vapor deposition (CVD) using tungsten hexafluoride (WF_6) and silane (SiH4) has been used to deposit tungsten (W) $^{1)}$ and tungsten silicide (WSi₂) ²⁾. Recently, it was discovered that W can be deposited on Si and metals by choosing the appropriate gas flow ratio for $SiH_4/WF_6^{(3)}$. Since then, selective W-CVD has been intensively investigated in terms of filling the submicron contacts and vias in silicon ultra-large-scale integrated circuits (Si-ULSIC). Despite these efforts, some problems still remain. The authors feel that selectivity loss is the most serious problem of selective W-CVD for practical application. Thus, an approach based on the selective W-CVD mechanism has to be pursued further to overcome this problem.

It has been widely believed for about ten years that SiF_4 and H_2 are the main by-product species in a chemical reaction between WF₆ and SiH₄⁴⁾. Recently, the surface reaction of selective W has been investigated using mass spectroscopy and X-ray photoelectron spectroscopy (XPS). Yu et al. concluded that the chemical reaction is expressed as $WF_6 + 3/2SiH_4 \rightarrow$ $W + 3/2SiF_4 + 3H_2$ ⁵⁾. Thus, this reaction has been accepted as the mechanism of selective W. In this work, selective W-CVD was investigated for the first time using *in-situ* Fourier transform infrared (FT-IR) spectroscopy and Auger electron spectroscopy (AES). The mechanism of selective W-CVD is clarified based on these experimental results.

2. Experimental

The experimental apparatus consisted of a preparation chamber, CVD chamber, and analysis chamber, as shown in Fig. 1. A 4-inch wafer was put on a molybdenum (Mo) holder and transferred among the three chambers using a magnetic-coupled transportation rod at a pressure of less than 10^{-5} Pa. In the CVD chamber, *in-situ* FT-IR spectroscopy was executed during W-CVD. The FT-IR spectra were obtained in the wavenumber range from 600 to 4200 cm⁻¹ for a resolution range of 0.5 - 4 cm⁻¹. An MCT (Hg1-xCdxTe) detector was used for high sensitivity measurements. Tungsten film was usually deposited on a 100-nm thick W film already sputter-deposited on a thermally oxidized wafer. Wafers with patterned oxides were also prepared to evaluate the selectivity of W deposition. The reaction gases on the wafer were quantitatively investigated by varying the following parameters within the ranges indicated: the gas flow ratio of SiH4/WF6 = 0.2-3.0, the total pressure = 40-130 Pa, the wafer temperature = $250-350^{\circ}C$, and the distance between the center of the IR beam (5 mm x 10 mm) and the wafer surface = 2.5-14.5 mm. The measurement apparatus is presented in Fig. 2.

The analysis chamber was equipped with a cylindrical AES spectrometer, a differential ion gun, and a quadropole mass spectrometer. The base pressure of the analysis chamber was 1.3×10^{-7} Pa when evacuated with an ion pump.

In this work, the relationship between gas pressure and IR absorbance was calibrated using pure WF_6 , SiH_4 , $SiHF_3$, and SiF_4 gases. Using the linear relationship obtained, the partial pressure of the reaction gases was measured from the IR absorbance.

3. Results and Discussion

The FT-IR spectra of the reaction gases indicate that $SiHF_3$ is the main byproduct species, and that SiF_4 is less than 20% of $SiHF_3$ for partial pressure, as shown in Fig. 3. Other fluoro-silane (e.g. SiH_3F and SiH_2F_2) and HF were not detected. The partial pressure of reaction gases on the W substrate is shown in Fig. 4. When W began to grow on the W substrate, the partial pressure of $SiHF_3$ and SiF_4 gradually increased while the partial pressure of SiH_4 decreased. Then, the partial pressure of SiH_4 , $SiHF_3$, and SiF_4 became constant with the deposition time. This corresponds to the constant deposition rate of W.

The W-CVD was carried out on a thermally oxidized silicon wafer. The partial pressure of the reaction gas is shown in Fig. 5. A comparison of the W-CVD on the W (Fig.4) and SiO_2 (Fig.5) makes it clear that the SiHF3 on the SiO2 substrate significantly decreased due to the small amount of W nucleation. In contrast, it should be noted that the partial pressure of SiF4 was only slightly influenced by whether the substrate material was W or SiO₂. When 0.4 < SiH4/WF6< 0.9, W was selectively deposited in the vias of a patterned wafer, and SiHF3 and SiF4 increased in proportion to On the other hand, when SiH4/WF6. $SiH_4/WF_6 = 3$, the W deposition became nonand SiHF3 increased in selective, proportion to SiH4/WF6. However, SiF4 did not increase and seemed to be saturated.

A W substrate was exposed to a gas flow of $SiH_4 = 15$ sccm for 5 min at 300°C. The total gas pressure was 100 Pa. AES analysis of the W surface detected these elements: Si (5.4 at%), W (57 at%), C (13 at%), and O (26 at%). It is noteworthy that a small amount of Si was formed on the W surface at a temperature as low as 300°C. These results strongly suggest that SiH4 dissociates to form Si when it absorbs on the W surface. The dissociation of SiH4 at the W surface can probably be expressed as

 $SiH_4(gas) \rightarrow Si(solid) + 2H_2(gas)$. (1)

In addition to the dissociation of SiH_4 , the dissociation of H_2 will occur, preferably at the W surface, as

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$$H_2 \rightarrow 2H$$
. (2)

The Si formed on the W surface will react with WF₆ and produce SiF, SiF₂, and SiF₃. The reaction pathway that produces SiHF₃ can be expressed as,

$$SiF_3 + H \rightarrow SiHF_3$$
. (3)

This model is favorably supported by an XPS study on a Si surface during dry etching using XeF_2 . It has been reported that SiF_3 was dominant among other radicals at the Si surface ⁶⁾.

4. Conclusions

The mechanism of selective W-CVD has been clarified. There exist two reaction pathways for selective W-CVD: [1] WF6(gas) + $2SiH_4(gas) \rightarrow W(solid) + 2SiHF_3(gas) +$ 3H₂(gas), and [2] WF₆(gas) + 3/2SiH₄(gas) \rightarrow W(solid) + 3/2SiF₄(gas) + 3H₂(gas). The chemical reaction of selective W-CVD is mainly expressed as Reaction [1]. Reaction [2] is not strongly influenced whether the substrate material is W or That is, it is a non-selective SiO2. chemical reaction. Considering the AES analysis of the W surface, the reaction pathway for SiHF3 formation is the surface reaction between dissociated H and SiF3.

These experimental results disprove the widely accepted model based on the assumption that SiF_4 is the main byproduct species. Moreover, they give us new guidelines for improving selectivity in applications of selective W-CVD.

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Fig. 1. Experimental apparatus for in-situ FT-IR spectroscopy and AES.



Fig. 2. Schematic figure of IR measurement apparatus in CVD chamber.



Fig. 4. Time dependence of partial pressure of reaction gases on W substrate (SiH₄/WF₆=5/20 sccm, 90 Pa).



Fig. 3. IR spectrum of reaction gases on W substrate (resolution = 4 cm⁻¹, 100 scans).



Fig. 5. Time dependence of partial pressure of reaction gases on SiO_2 substrate $(SiH_4/WF_6=5/20 \text{ sccm}, 90 \text{ Pa})$.