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Study of chemical vapor deposition reaction between tungsten hexafluoride and silicon difluoride

Chi-Young Lee and Wen-Chung Yang

Materials Science Center, National Tsing Hua University, Hsinchu, Taiwan, R.O.C. E-mail: cylee@msc.nthu.edu.tw

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A low-pressure chemical vapor system which deposits tungsten based thin films on a substrate, using a horizontal hot-wall reactor has been studied. WF_6 and SiF_2 were used as precursors to deposit materials containing tungsten, at temperatures between 100 and 800 °C. Results demonstrate that a deposition temperature below 400 °C led to polycrystalline tungsten and silicon oxide. Tungsten films deposited at higher temperature (300–400 °C) were normally present in the α structure while for those tungsten films deposited at lower temperature ($<$300 °C), XRD patterns indicated mixed α and β phases. As the reaction temperature was increased to $\geqslant$500 °C, polycrystalline tungsten silicide and polycrystalline silicon were deposited on the surface of the substrate. This study investigates the effect of different processing conditions for forming W and WSi_2 and the role of SiF_2 in their formation.

Introduction

According to the literature, WF_6 can be thermally decomposed above 750 °C to obtain tungsten metal.[1] Most methods to reduce the reaction temperature of tungsten CVD require reducing agents such as H_2, Si, SiH_4, Si_2H_6, B_2H_6, PH_3, SiH_2Cl_2 and GeH_4. H_2, Si and SiH_4 are the agents most often used in the integrated circuits fabrication processes.[2]

Reducing tungsten hexafluoride using a silicon substrate allows selective tungsten deposition on silicon without deposition on other substrates. Unfortunately, the reaction stops after a few seconds before it can create a critical thickness of the tungsten layer.

Hydrogen, at a temperature of between 300 and 800 °C, can also reduce tungsten hexafluoride. Reducing WF_6 using hydrogen is an endothermic process driven by entropy considerations. However, the reaction product, HF, can cause encroachment into films and formation of wormholes.

Use of a reducing silane to deposit tungsten has attracted attention, because a higher deposition rate is possible using this method, leading to fewer wormholes, less encroachment, and less consumption of silicon.

In 1989, Pauleau *et al.* reported the deposition of tungsten silicide and molybdenum silicide thin films by using difluorosilylene and hydrogen as a reducing atmosphere.[3] We have reported that thin films of $TiSi_2$ and $TaSi_2$ can be made by the reaction of SiF_2 and Ti and Ta halides at very low temperature. It is also known that silylene is a good precursor for the preparation of silicon-containing thin films.[4,5]

In this study, we report the reaction of tungsten hexafluoride and silicon difluoride at different reaction temperatures. At temperatures $\leqslant$400 °C, this reaction deposited tungsten on the substrate surface, but on increasing the temperature to $\geqslant$500 °C, tungsten silicide was deposited.

Experimental

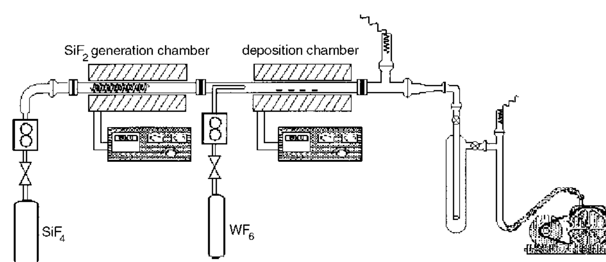
(a) General description of the experimental procedure

Deposition reactions were performed in a low-pressure hot wall reactor. The reactor consisted of a pumping system, a reaction chamber, a precursor inlet system and a system for generating SiF_2, as shown in Scheme 1. The reactor included a removable quartz tube (30 mm inside diameter), connected to a SiF_2 generation chamber. The reaction of SiF_4 and Si, packed inside the generation chamber at 1150 °C, generated SiF_2 with an approximate yield of 50%.[6] Substrates used here were silicon wafers, graphite and SiO_2. (Thin films grown on graphite substrates were used for composition measurement.)

WF_6 (Strem) and SiF_4 (Matheson) were used as received from the suppliers. Grease was removed from the silicon substrates using standard RCA procedures;[7] the oxide was etched off the substrates just before loading. The quartz substrates were washed with household detergent, rinsed with distilled water, and then dried at 120 °C for 10 min. The reaction and substrate temperatures were measured using a K-type TC gauge. The amounts of WF_6 and SiF_4 inlet were measured using mass flow controllers.

Deposition runs were conducted according to the following general procedure: (1) The system was evacuated to a pressure of 10^{-2} Pa. (2) The reactor and the SiF_2 generation chamber were heated to the desired temperatures. (3) The system was evacuated to 10^{-3} Pa. (4) SiF_4 gas, at room temperature, was introduced into the SiF_2 generation chamber. (5) 0.5 $cm^3\ s^{-1}$ (STP) of WF_6, at room temperature, was introduced into the reactor. (6) Controlled deposition temperatures between 100–800 °C were applied for 2 h. (7) The samples that were deposited at reaction temperatures $\geqslant$500 °C were heated to 800 °C to anneal the films. (8) After reaction, the samples were removed from the reaction chamber and exposed to the air.

The volatile products that were collected by the liquid nitrogen trap were analyzed by IR and mass spectra. The morphology of the thin films was characterized by scanning



Scheme 1

electron microscopy while the composition of the thin films was analyzed by energy dispersive spectroscopy. The microstructure of the thin films was analyzed by X-ray diffraction while X-ray photoelectron spectroscopy was used to characterize the chemical composition of the thin films. Auger electron spectroscopy was used to obtain depth composition profiles of the thin films.

(b) Characterization of the reaction products

SEM micrographs were obtained using a JEOL 840A SEM microscope with energy dispersive spectroscopy (EDS) analytical capability. X-Ray diffraction (XRD) patterns of the thin films were measured using Cu-Kα radiation, on a Siemens D5000 diffractometer. IR spectra were obtained using a Perkin-Elmer PC2000 IR spectrometer. GC–MS data were obtained using a Shimadzu QP1000 spectrometer. X-Ray photoelectron spectra (XPS or ESCA) were measured on a Physical Electronics PHI 1600 ESCA spectrometer. Auger electron spectra were measured on a Physical Electronics 670 PHI Xi Auger spectrometer.

Results and discussion

Using tungsten hexafluoride and silicon difluoride as precursors, the deposition reactions were conducted between room temperature and 800 °C. At room temperature the reactions yielded a dark blue deposit on the reaction wall upon mixing of the reagents. The reaction led to dark gray metallic thin films on quartz and silicon wafers as the temperature was increased to >100 °C. Results indicated that the thin films adhered well to the substrate surface (according to a Scotch tape test). The composition of thin films, as analyzed by EDS and Auger spectroscopy, depended upon the temperature. At lower reaction temperatures (100–400 °C), tungsten (60–80 atom%) was the major component of the thin films. AES survey spectra also confirmed the composition of thin films (Fig. 1). At a higher reaction temperature (500–800 °C), the major components of the thin films were silicon and tungsten disilicide. Tables 1 and 2 list the thin film properties, block compositions and reaction conditions.

Fig. 2 illustrates the high-resolution X-ray photoelectron spectra of the W 4f and Si 2p regions in thin films deposited on silicon wafers at 150 °C. The binding energies of W $4f_{7/2}$ at 30.8 eV and W $4f_{5/2}$ at 33.0 eV , were assigned to elemental W;

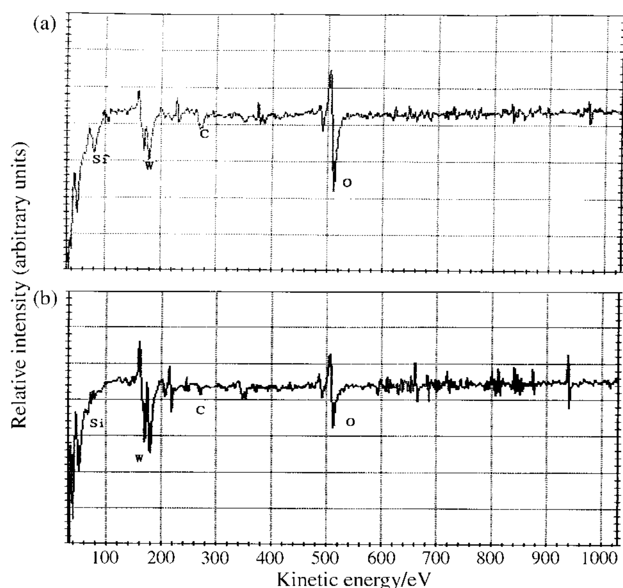


Fig. 1 Auger electron survey spectra of a thin film deposited at 200 °C, (a) examined before sputtering and (b) examined after sputtering.

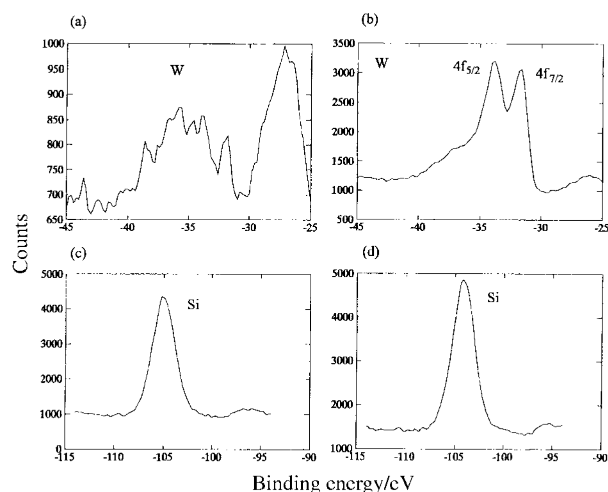


Fig. 2 Typical W 4f and Si 2p binding energy spectra of a thin film deposited at 150 °C: (a) and (c) examined before sputtering and (b) and (d) examined after sputtering.

Si 2p at 103.5 eV can be assigned to SiO_x($x=0.2$–0.7).[8] As the reaction temperature was increased to $\geqslant 500$ °C, the binding energies of W $4f_{7/2}$ at 30.6 eV, W $4f_{5/2}$ at 33.3 eV, and Si 2p at 99.6 eV can be assigned to W and Si atoms in an –Si–W– network, or in a mixture of tungsten and silicon.

X-Ray diffraction pattern measurements show that films grown at temperatures of $\leqslant 400$ °C are composed of polycrystalline W, whereas films grown at temperatures of $\geqslant 500$ °C are a mixture of polycrystalline silicon and polycrystalline tetragonal WSi_2. Fig. 3 shows X-ray diffraction patterns of the thin gray films grown on quartz substrates at different deposition temperatures. The major 2θ(Cu-Kα) peaks were at 35.7, 40.37, 44.0, 58.38, 73.47 and 87.51° and are comparable to the XRD angles of α- and β-tungsten: the former shows (110), (200), (211) and (220) reflections at 2θ 40.26, 58.27, 73.19 and 87.02° while the latter shows (200) and (211) reflections at 2θ 35.3 and 43.9°.[9] The results indicated that the tungsten films deposited at higher temperatures (300–400 °C) are generally present in the α structure; whilst those deposited at lower temperatures (<300 °C) show XRD patterns corresponding to both α and β phases. The X-ray diffraction patterns of a thin film grown on graphite at 700 °C (Fig. 4) show major 2θ(Cu-Kα) peaks at 2θ 26.40, 28.43, 30.00, 39.66, 42.41, 44.61, 46.17, 47.39, 54.42, 56.35, 62.46, 77.47 and 83.53°. These peaks can be compared with those of the graphite substrate, Si and WSi_2: graphite displays reflections at 2θ 26.5, 42.4, 54.64, 77.40 and 83.53°, Si at 2θ 28.43, 47.39 and 56.11° and WSi_2 shows (101), (110), (103), (112) and (202) reflections at 2θ 30.06, 39.66, 44.84, 46.24 and 62.48°.[10]

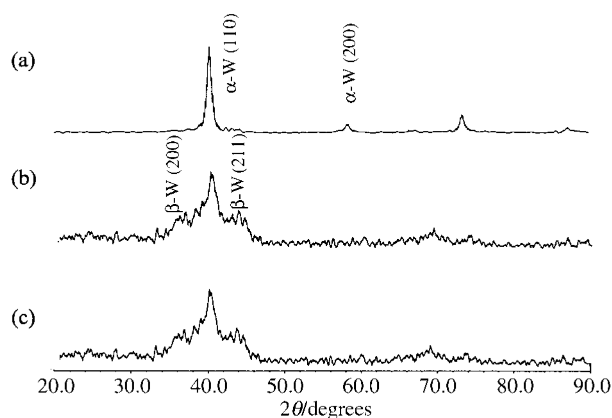
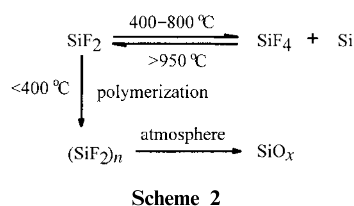


Fig. 3 Powder X-ray diffraction patterns of thin films grown on quartz at different reaction temperatures (a) 300 °C, (b) 200 °C and (c) 100 °C.

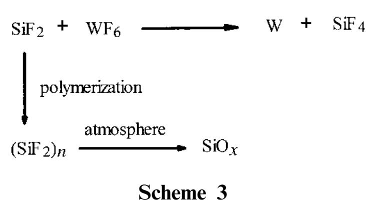
Table 1 Composition of deposited films as a function of deposition temperature and $WF_6:SiF_2+SiF_4$ flow ratio in the range 100–400 °C[a]

Deposition temperature/°C	Flow ratio ($WF_6:SiF_2+SiF_4$)	% Composition (EDS) W	Si	O
100	1:6	72	14	10
	1:7	64	18	14
200	1:6	68	12	14
	1:7	70	10	12
300	1:6	68	18	10
	1:7	80	10	8
400	1:6	78	12	8
	1:7	60	30	7

[a]The microstructure is polycrystalline tungsten.



Scheme 2



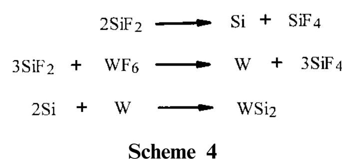
Scheme 3

The volatile product in all the reactions was entirely silicon tetrafluoride (SiF_4).

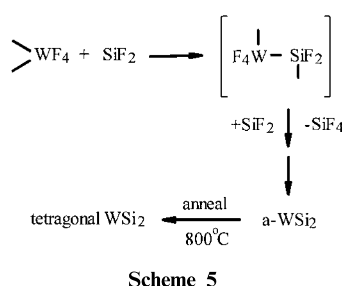
Difluorosilylene (SiF_2) is known to disproportionate to SiF_4 and Si at 650 °C. This study showed that the optimum temperature range for depositing Si from SiF_2 was 400–800 °C[10] and the fastest growth rate for silicon thin films occurred at 650 °C. At ⩽400 °C, silicon oxide (SiO_x) was the only silicon product that formed on the substrate surface. Silicon oxide forms because polymerization of SiF_2 leads to $(SiF_2)_n$ which, upon exposure to the air, forms silicon oxide (Scheme 2).

WF_6 and SiF_2 react to form polycrystalline tungsten and silicon oxide at reaction temperatures of ⩽400 °C. Under these conditions SiF_2 acts as a reducing agent, reducing WF_6 to W, while a competitive reaction is the polymerization of SiF_2. The yield of the polymerization product, SiO_x, seems to bear no relation to the reaction temperature or to the inlet ratio of $WF_6:SiF_2$. The entire reaction can be described by Scheme 3.

At reaction temperatures of ⩾500 °C, polycrystalline silicon and tungsten silicide were deposited on the substrate surface. As is generally known, polycrystalline tungsten silicide is formed by two different processes: a solid-state reaction between tungsten and silicon at *ca.* 1200 °C and a chemical reaction leading to amorphous tungsten silicide, which is then annealed to form polycrystalline tungsten silicide. In this study, WF_6 and SiF_2 also lead to polycrystalline tungsten silicide from a solid-state reaction and a chemical reaction. If silicide thin films form by the solid-state reaction of W and Si, as reported in the literature, the reaction pathway can be described by Scheme 4.



Scheme 4



Scheme 5

The disproportionation of SiF_2 leads to Si, while WF_6, reduced by SiF_2, leads to W, enabling tungsten silicide to grow at high temperatures. For this to occur, the annealing temperature should be above the solid-state reaction temperature for WSi_2, of 1200 °C.[11] However, in this study, the annealing temperature was only 800 °C, far below the solid state reaction temperature for tungsten and silicon. It thus appears that the solid-state reaction pathway does not fit the experimental data. Thus, we postulate here that the reaction pathway for the formation of tungsten silicide is, initially, insertion of SiF_2 into a W–F bond of WF_6 (followed by the defluorination of the intermediate by SiF_2) leading to amorphous tungsten disilicide and SiF_4. This reaction is shown in Scheme 5.

According to the blank reaction of SiF_2, we know that a disproportionation reaction occurs for SiF_2 between 400 and 800 °C.[4,12] However, in the reaction between SiF_2 and WF_6, polycrystalline silicon is obtained only at temperatures between 500 and 800 °C with no polycrystalline silicon obtained at 400 °C. These results indicate that the disproportionation reaction does not compete with the reduction reaction at ⩽400 °C. As the temperature is increased to >500 °C, the disproportionation reaction becomes dominant, and is accompanied by the insertion of SiF_2 into a W–F bond of WF_6. This

Table 2 Composition of deposited films as a function of deposition temperature in the range 500–800 °C[a]

Deposition temperature/°C	Flow ratio ($WF_6:SiF_2+SiF_4$)	Tungsten:silicon ratio W:Si (EDS)
500	1:4	0.16
600	1:4	<0.01
700	1:4	<0.01
800	1:2	0.05

[a]The microstructure is polycrystalline tungsten silicide and polycrystalline silicon.

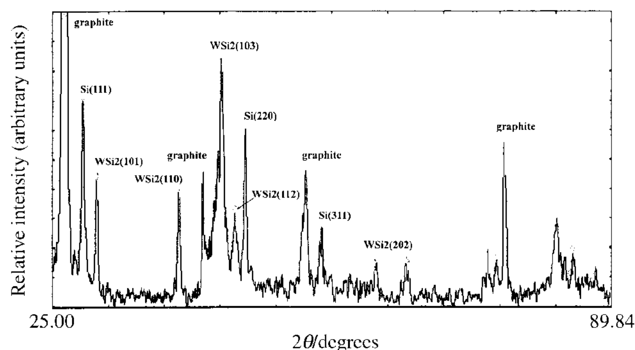


Fig. 4 Powder X-ray diffraction pattern of a thin film grown on quartz at 700 °C and then annealed at 800 °C for 1 h.

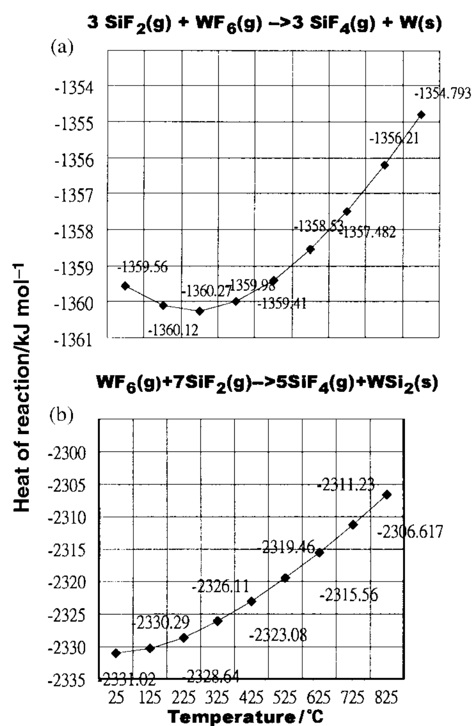


Fig. 5 The estimated heat of reaction of formation for (a) tungsten and (b) tungsten silicide at different reaction temperatures.

insertion reaction is essential for silicide formation. According to analysis of the bulk composition of the thin films prepared at temperatures ⩾500 °C, the amount of silicon contained in the thin films is related to the deposition temperature. These results are consistent with the growth rate of silicon by a disproportionation reaction.

According to a thermodynamic analysis of these reactions, the formation of tungsten silicide is a more favorable reaction than that of tungsten metal.[13] The heat of reaction of formation of tungsten and tungsten silicide at different reaction temperatures are shown in Fig. 5.

In summary tungsten films were obtained at low temperatures and tungsten silicide films were obtained at high temperatures. These results imply that tungsten metal thin films are obtained as a kinetic product, upon reduction of WF_6 by SiF_2, and tungsten silicide thin films were obtained as a thermodynamic product by insertion of SiF_2 into WF_6.

Conclusions

WF_6 and SiF_2 have been used as precursors, in a low-pressure chemical vapor deposition reactor, to prepare tungsten related thin films under various deposition conditions. A polycrystalline cubic tungsten deposit was obtained at deposition temperatures of ⩽400 °C. As the reaction temperature was increased to ⩾500 °C, a mixture of polycrystalline tungsten silicide and polycrystalline silicon was obtained on the surface of the substrate. Results indicate that the lowest deposition temperature is 100 °C for W and 500 °C for WSi_2. We found that tungsten metal thin films were obtained as a kinetic product and tungsten silicide thin films as a thermodynamic product. Using this reaction to obtain tungsten-based thin films has the following advantages over other methods: a low reaction temperature; no hydrogen, silane, or HF gas used or produced; and less consumption of silicon substrate.

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