# Characterization of Selective Tungsten Films Prepared by Photo-Chemical Vapor Deposition

## Y. K. Fang, S. B. Hwang, and C. Y. Sun

VLSI Technology Laboratory, Research Institute of Electronics and Electrical Engineering, National Cheng Kung University, Tainan, Taiwan, China

## ABSTRACT

Selective photo-chemical vapor deposition (CVD) of tungsten films decomposed by direct photoexcitation of  $WF_6$  have been studied. Film deposition rate increased with increasing temperature but was only slightly dependent on  $WF_6$  gas concentration. The selectivity deteriorated with increasing deposition temperature,  $WF_6$  concentration, and deposition time. Typically, in order to achieve selectivity, the flow rate of  $WF_6$  must be lower than 35 sccm and the deposition temperature must be lower than 230°C. No encroachment and self-limited thickness problems were found as in the low-pressure chemical vapor deposition method. In general, tungsten films prepared by photo-CVD were amorphous as observed by x-ray diffraction analysis. After annealing, the tungsten had a polycrystalline structure with a resistivity of 18  $\mu\Omega$ -cm.

As a refractory metal, tungsten has several desirable properties, such as high melting point, high reaction temperature with silicon, low electrical resistivity, low reactivity with aluminum, and high resistance to electromigration (1, 2). These properties, coupled with the ability to be selectively deposited using CVD, provide for the possibility of producing a number of self-aligned structures. In the past, the selective low-pressure chemical vapor deposition (LPCVD) (3-10) of tungsten involved the formation of a tungsten layer on the exposed surfaces of silicon, aluminum, and various metal silicides without the tungsten forming on SiO<sub>2</sub>. These results in a self-aligned tungsten pattern which does not require a lithographic masking step and, consequently, is an attractive option for a number of integrated circuit applications (3). However, in the LPCVD method, some undesirable side effects are found during the deposition. For example, during selective deposition of tungsten, using a  $WF_6$  + Ar gas mixture, W is deposited by the silicon reduction of  $WF_6$ . Silicon atoms from the substrate are consumed in the reaction, hence, encroachment often happens at the SiO2/Si interface. Also the deposited W layer will interrupt the continuous silicon reduction of  $WF_6$ . Thus, only a thin tungsten layer can be obtained due to this self-limiting property. Another method often used for selective deposition of tungsten is hydrogen reduction of  $WF_6$  gas. During the reaction, a byproduct, HF, is generated, and is incorporated with the grown tungsten into the silicon substrate and consequently reacts with silicon.

In this study, the tungsten film is produced by direct decomposition of  $WF_6$  by photoexcitation above the Si substrate. Consequently, no HF is generated, and the chance for  $WF_6$  reaction with Si substrate is reduced. Thus, both the self-limiting thickness and encroachment problems (11) are eliminated automatically, although there still exists a problem of silicon consumption which, fortunately, is inhibited by the self-limiting effect (1). Also, the present authors study the compatibility of tungsten selective photo-CVD on Al/Si contact system for VLSI application.

## **Experimental Technique**

The deposition of tungsten films was carried out in a photo-CVD system. The system is a vertical-type LPCVD system equipped with an ultraviolet light source array as illustrated in Fig. 1. The source generates a UV light with peak intensity at 253.7 nm (corresponding to an energy of 4.886 eV) and power density of 12 mW/cm<sup>2</sup>. With the aid of the UV light energy, tungsten films can be deposited by the following reactions (12, 13)

$$\begin{split} H_{g}(^{1}S_{o}) + h\gamma(4.886 \text{ eV}) \rightarrow H_{g}^{*}(^{3}P_{1}) \\ H_{g}^{*}(^{3}P_{1}) + WF_{6} \rightarrow W + 3F_{2} + H_{g}(^{1}S_{o}) \end{split}$$

where  $H_g(^1S_o)$  and  $Hg_g^*(^3P_1)$  are the ground and excited states of mercury atoms, respectively. To maintain a con-

stant pressure in the reactor (1 torr), Ar gas is introduced into the chamber. N-type, (100)-oriented, single-crystal silicon wafers, with 4-7  $\Omega$ -cm resistivity, are used as substrates. The gas flow rate and partial pressures of WF<sub>6</sub> and argon are varied as given in Table I.

The thickness of deposited W is measured by a stylus profilometer and examined by scanning electron microscopy (SEM).

## **Experimental Results and Discussion**

Figure 2 shows the W film deposition rate as a function of the flow rate of  $WF_6$  at various deposition temperatures. The deposition time is fixed at 20 min. The deposition rate of W increases with increasing deposition temperature and is slightly affected by the concentration of  $WF_6$ . In Fig. 3 the thickness of W deposited at  $230^{\circ}$ C is plotted as a function of deposition time at various flow rates of  $WF_6$ . The self-limiting thickness phenomenon encountered in conventional LPCVD or CVD (1, 11) is not observed. Instead a saturation thickness saturation could be attributed to the coating of the optical window with tungsten during deposition time, thus leading to a decrease in the introduction of UV light into the reactor.

In these experiments, selective deposition tungsten films on oxide-patterned silicon wafers have been successfully reproduced. However, it was found that selectivity deteriorated with increasing deposition time and temperature. The tungsten can be grown selectively within a deposition time of 40 min at 230°C or 30 min at 300°C. Above 400°C, selectivity is completely lost.

As stated earlier, in conventional W CVD processes, either Si atoms of the substrate are consumed during the re-



Fig. 1. Schematic diagram of mercury-sensitized photo-CVD apparatus.

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Table I. Process parameters for selective tungsten deposition.

	WF <sub>6</sub>			Ar	Total
Flow rate	35	100	160	120-300	
(mtorr)	20	55	90		1000

duction of WF<sub>6</sub>, thus leading to encroachment at the SiO<sub>2</sub>/Si pattern edge (11), or the hydrogen reduction, leads to the production HF, and consequently causes a wormhole problem (5). However, in the photo-CVD system, these problems are suppressed completely. Figure 4 shows SEM micrographs of tungsten selectively deposited onto oxide-patterned silicon at 230°C as a function of WF<sub>6</sub> flow rates. Figures 4a and b show no significant encroachment occurring with a flow rate of WF<sub>6</sub> at 35 sccm in which Fig. 4a is a top view and Fig. 4b is a cross-section. In contrast, Fig. 4c shows encroachment at the SiO<sub>2</sub>/Si interface, when a larger flow rate of WF<sub>6</sub>, e.g., 100 sccm, is employed.

The SEM micrographs show that the tungsten surface, deposited at 230°C with a WF<sub>6</sub> flow rate of 35 sccm, is



Fig. 2. W films deposition rate as a function of the flow rate of  $WF_6$  with various deposition temperatures as parameter. Total deposition pressure = 1 torr.











Fig. 4. SEM micrograph of SiO<sub>2</sub>/Si interface (a, top) the flow rate of WF<sub>6</sub> is 35 sccm, (b, middle) cross-section of (a), and (c, bottom) the flow rate of WF<sub>6</sub> is 100 sccm.

smooth and dense with very tiny tungsten particles. The as-deposited tungsten films are amorphous as examined by x-ray, shown on Fig. 5, and have resistivities around 100-120  $\mu\Omega$ -cm. Upon annealing at high temperature, the resistivities reduce due to phase changes and grain growth (14). As shown in Fig. 6 the resistivity can be reduced to 18  $\mu\Omega$ -cm with a 800°C anneal in Ar gas atmosphere for 30 min. In these measurements of tungsten film thicknesses were kept at 5000 Å.

To investigate the compatibility of selective photo-CVD tungsten with an aluminum/silicon contact system, a 1000 Å photo-CVD tungsten film was selectively deposited into a contact hole on a 0.01  $\Omega$ -cm, (100)-oriented, N<sup>+</sup>-type Si wafers with 3.3  $\Omega$ -cm epitaxial N-type layer. The contact hole was first patterned by SiO<sub>2</sub> with area of 7.85  $\cdot$  10<sup>-3</sup> cm<sup>2</sup>,



Fig. 5. X-ray diffraction of 230°C as-deposited tungsten film.



Fig. 6. Variation in resistivity as a function of annealing temperature for 30 min in Ar ambient.

30 min. After that, a 6000 Å Al film was evaporated and defined on the top of the annealed W film. Finally, the Al/W/Si Schottky system was annealed, just analogous to the sintering process of the Al layer in very large scale integrated (VLSI) multilayer applications, as the last layer to provide electrical interconnections. The measured Al film sheet resistance, R, as a function of annealing temperature with normalization to as-deposited sheet resistance,  $R_o$ , is shown in Fig. 7. These samples have been annealed in Ar gas for 30 min.

The sheet resistance value of the Si/W/Al samples is constant up to an annealing temperature of  $450^{\circ}$ C, then increases significantly beyond  $550^{\circ}$ C. These observations were supplemented by Schottky barrier measurements. Figure 8 shows the Schottky barrier height of the Si/W/Al contact vs. annealing temperature. For annealing temperature lower than  $450^{\circ}$ C, the barrier of Si/W/Al Schottky diode is maintained at a constant value of 661 mV. Above  $550^{\circ}$ C, the barrier height increases quickly. In addition, Fig. 9 shows the change of barrier height during isothermal annealing at  $450^{\circ}$ C. A constant barrier height is found. Furthermore, possible mercury contamination of the tungsten film is a concern in VLSI applications. However, as shown on Fig. 10, the Auger electron spectrum of



Fig. 7. Normalized sheet resistance ( $R/R_o$ ) of the Si/W/Al samples as a function of annealing temperature (30 min),  $R_o$  is 0.5  $\Omega/\Box$  for all samples.



Fig. 8. Barrier height of Si/W/AI Schottky diode as a function of annealing temperature.



Fig. 9. Barrier height of Si/W/AI Schottky diode as a function of annealing time for 450°C annealing temperature.

photo-CVD tungsten film, no detectable amounts of mercury impurity are observed, except the small quantity of oxygen and carbon, which appear to be due to the native oxide and ambient conditions.

The results show that selective photo-CVD is a satisfactory process for the production of tungsten films for applications as a diffusion barrier layer between Al electrodes and Si substrates in VLSI applications.

### Summary

Tungsten films have been selectively deposited successfully on oxide-patterned silicon at very low temperature

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Fig. 10. The Auger electron spectrum of as-deposited W film.

(230°C) by the mercury-sensitized photo-CVD method. All films are pure, conformal, and smooth as examined by SEM. The selective growth of the tungsten film is strongly affected by substrate temperature, and to a much lesser degree by the concentration of  $WF_6$ . The optimized substrate temperature is about 230°C, and selectivity is lost above 400°C. With photo-CVD growth, both the wormhole and encroachment problems are suppressed. The as-deposited film is amorphous with resistivity around 100-120  $\mu\Omega$ -cm, which is reduced to 18-20  $\mu\Omega$ -cm after annealing at 800°C in Ar ambient. Also, the photo-CVD selectively produced tungsten can be used as a diffusion barrier in Al/Si contact up to 450°C. In this case, both the sheet resistance and barrier height are constant. This means that selective photo-CVD is a satisfactory process for the production of tungsten films for applications as a diffusion barrier layer between Al electrode and Si substrate in VLSI applications.

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# The APCVD Growth of PSG and BPSG Films Using Tertiarybutylphosphine as a Phorphorus Dopant

Giorgio U. Pignatel

Department of Electrical Engineering, University of Bari, Bari, Italy

## Joe C. Sisson

Watkins-Johnson Company, Scotts Valley, California 95066

#### Wayne P. Weiner\*

American Cyanamid Company, Wayne, New Jersey 07470

#### ABSTRACT

The use of a less hazardous alternative to phosphine gas, tertiary butylphosphine (TBP), has been investigated for the growth of phosphosilicate and borophosphosilicate films in an atmospheric pressure chemical vapor deposition reactor (APCVD). Data on film growth rate, composition, stress properties, and refractive index are reported. The results indicate that TBP serves as a viable alternative to phosphine gas in the APCVD growth of doped silicate glasses.

Borophosphosilicate (BPSG) and phosphosilicate (PSG) films are ubiquitous in the fabrication of semiconductor devices. These films have a variety of applications, but are most commonly used as dielectric layers or final passivation coatings. The films can be deposited by a number of techniques. One common method is the atmospheric pressure chemical vapor deposition process (APCVD) using silane, phosphine, diborane, and oxygen (1).

As the sensitivity toward the use of toxic, compressed gases increases, interest is being focused on viable alterna-

used extensively for the metal oxide chemical vapor deposition (MOCVD) growth of InP materials (3), as a phosphorus source in ion implantation processing (4), and in the growth of phosphorus in situ doped polysilicon films (5). In light of the success of using TBP in these applica-

tives to these materials which are less hazardous to labora-

tory personnel and the surrounding community (2). Over

the last several years, the use of a liquid alternative to phosphine gas, tertiarybutylphosphine (TBP), has been

tions, it was of interest to study the use of TBP as a replacement for PH<sub>3</sub> in the growth of PSG and BPSG films.