# The Study of W Deposition on Si Substrate by $SiH_4$ Reduction of $WF_6$ in LPCVD System

Sung Hoon Kim, Se Ahn Song[+], and Seong Keun Kim[*]

*Department of Chemistry, Seoul National University, Seoul 151-742*

*[+]Department of Materials Devices Research Center, Samsung Advanced Institute of Technology, P.O Box 111,Suwon 440-600*

## Introduction

Refractory metals(W, Mo, etc.) are very promising materials for VLSI applications such as interconnect lines, diffusion barriers and gate materials because they exhibit lower electrical resistivity, higher electromigration resistance and better thermal stability than aluminum or other materials. Recently, W deposition on Si substrate has been widely investigated as a substitute for Al and poly-Si. In this study, to prepare W films of good characteristics, we deposited W on Si substrate by $SiH_4$ reduction of $WF_6$ in LPCVD system by using both cold-wall and pseudo hot-wall reactors. In cold-wall case we were able to determine film growth mode. We also studied film structure and characteristics through analyses of physical properties and composition of the film. The deposited W film was annealed and the change in structure and characteristics were investigated.

## Experimental

The LPCVD system of cold-wall type in this work is a single wafer process type with inlet ports for different source gases. The temperature of the substrate was uniformly maintained during the reaction process by a resistance heater with a temperature controller. The reaction temperature was set constant at 450°C. The pseudo hot-wall reactor condition was met by installing a stainless steel shield (17cm × 17cm × 26cm) around the heater and sample. Annealing was performed at 800°C for 30 min in vacuum. By using a home-made in-situ surface monitor that consists of a He-Ne laser and photodiode detector with a monochromator, the change in film thickness was monitored as the reaction proceeded. P-(100) 10mm Si wafers were used as substrate. They were pretreated with 10% HF buffer solution for 1 min. and dried with nitrogen gas before reaction. $WF_6$(99.999%) was used as reactant gas and $SiH_4$(99.999%) as reduction gas. No buffer gas was used. Flow rates of $WF_6$ and $SiH_4$ were each maintained at 36 sccm(standard $cm^3$/min) and 18 sccm by mass flow controller. Images of film surface and cross section were examined by SEM(scanning electron microscopy) and TEM(transmission electron microscopy). Film thickness was measured also by SEM, TEM, and a stylus-type device(Dektak). Electrical resistivity was measured by a four point probe. Composition of film was determined by EDX(energy dispersive x-ray microanalysis) and Auger spectroscopy. XRD(X-ray diffraction) and SAED(selected area electron diffraction) pattern from TEM were used to obtain crystallographic structure of the film.

## Results and Discussion

**Deposition step.** To determine whether the W deposition proceeds in one step(Si substrate reduction or $SiH_4$ reduction) or in two steps(Si substrate reduction and the following $SiH_4$ reduction), we deposited W with four different types of souce gas, i.e., $WF_6$ only(case 1), $SiH_4$ only(case 2), $WF_6$ + $SiH_4$(case 3) and $WF_6 \rightarrow SiH_4 \rightarrow WF_6 + SiH_4$(case 4). By using the in-situ surface monitor, the incubation period and the the trend for change in surface was observed. We found that in case 2 no Si or $SiH_x$ are deposited but in cases 1,3, and 4 the same initial reaction (Si substrate reduction of $WF_6$) takes place. This initial reaction produces a very thin film(~300Å) whose growth is self-limited. The SEM micrograph of Si substrate surface with W film peeled off gives some indication that chemical reaction has taken place between Si substrate and $WF_6$. This assumption is supported by the observed roughness of the interface between W and Si layers. Based on the above results, we propose that the W deposition in $SiH_4$ reduction reaction proceeds by initial Si substrate reduction of $WF_6$ and the following $SiH_4$ reduction of $WF_6$.

**Film growth mode.** After the initial growth by substrate reduction of $WF_6$, new W layers are produced by $SiH_4$ reduction of $WF_6$. Small critical nuclei are first formed at binding sites because of very high binding energy(5.83 eV) between W atom and W substrate, which produces a very fine surface image. As more W nuclei are produced by $SiH_4$ reduction of $WF_6$, deposited W nuclei are partially aggregated. As a result, islands are formed at binding sites. As the reaction proceedes the W islands coalesce together, with a resulting increase in size, and also additional new islands are formed. The overall film growth is observed to follow the Volmer- Weber mode.

**Film structure, characteristics and the effect of annealing.** The deposited film shows mostly the α-W structure which is of BCC type. The growth rate for the case 3 is ~300Å/min. W films produced by the displacement reaction has a much smoother surface than those from $SiH_4$ reduction reaction. This is probably caused by the more heterogeneous character of the former process and thus a smaller grain size. The electrical resistivity values are ~15μΩ-cm in case 1 and 3. Annealing at 800°C produced a film with a much more even concentration of W over the entire substrate, but no structural change was observed. The electrical resistivity dropped slightly to ~13μΩ-cm as a result of annealing.

**Comparison of films prepared by cold-wall and pseudo hot-wall reactors.** Films were also produced by pseudo hot-wall reaction and the growth rate was found to be much higher(~3000Å/min) than that from the cold-wall reaction(~300Å/min). The XRD data showed only W(110) and W(200) structures for these films but 800°C annealing gave strong XRD peaks at $WSi_2(002)$, $WSi_2(101)$,and $WSi_2(112)$ positions. To analyze the composition of the film from pseudo hot-wall reaction, AES analysis was carried out, which revealed a higher oxygen and silicon content compared with cold-wall case. The film surface of pseudo hot-wall reaction is found to be much more rough than that of cold-wall reaction. The electrical resistivity value of the pseudo hot-wall film was much higher(~100μΩ-cm) than those of cold-wall film in both as-deposited and 800°C annealed cases.

## Conclusions

We deposited W film on Si substrate by $SiH_4$ reduction of $WF_6$ in LPCVD system under both cold-wall and pseudo hot-wall conditions. W is deposited by a two-step reaction, i.e., Si substrate reduction and the subsequent $SiH_4$ reduction of $WF_6$. W film was grown in Volmer-Weber mode. The deposited film is known to have an α-W structure which is of BCC type with a more stable form and lower resistivity than β-W. Annealing at 800°C resulted in a more even concentrationof W and a slightly lower electrical resistivity. The pseudo hot-wall reaction produced films of much higher thickness, but a lower film quality and a much higher electrical resistivity as well.