Chemical vapour deposition of tungsten by H₂ reduction of WCl₆

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Tungsten chemical vapour deposition in a cold wall reactor using WCl₆ as tungsten source has been investigated. Film growth on silicon substrates by H₂ reduction of WCl₆ has been studied at atmospheric pressure and at a pressure of 40 Torr in the temperature range 480 to 670°C. Deposition at atmospheric pressure is limited by transport of reactants to the growth surface, resulting in non-uniform films with rough surfaces. At 40 Torr smooth films are obtained and growth rates are 10 to 110 nm/min. Resistivities are 8 to 17 μΩ-cm in the film thickness range of 100 to 800 nm. These values are comparable to those obtained in the WF₆/H₂ process. However, reproducibility of the process is poor. Tungsten can also be deposited on Mo, TiN and W surfaces from WCl₆/H₂ gas mixtures. In absence of hydrogen tungsten films are etched by WCl₆. Thermodynamic calculations predict the formation of tungsten subchlorides in this reaction.

1. Introduction

Tungsten offers several advantages for use in metallization of very large scale integrated circuits. Tungsten film deposition from WF₆ in LPCVD processes has been studied extensively and properties of the films produced by silicon or hydrogen reduction of WF₆ have been characterized and reviewed in the literature [1–3]. However, the fluoride-based processes have several disadvantages resulting from the reactivity of WF₆ and the reaction product HF towards the silicon substrate and silicon dioxide, causing encroachment, formation of wormholes and selectivity loss. Alternatively, fluorine-free tungsten compounds may be applied as precursors in CVD processes without these disadvantages.

The applications of tungsten chlorides in tungsten coating of tubes, wire and particles have been reviewed by Powell et al. [4]. Vapour deposition by pyrolysis of tungsten pentachloride (WCl₅) or tungsten hexachloride (WCl₆) has been performed at temperatures ranging from 1200 to 2400°C. Tungsten formation by hydrogen reduction of tungsten chlorides is possible at considerably lower temperatures (600–900°C). At these temperatures WCl₆ is more easily reduced than WCl₅.

Mehalchick and MacInnis [5] used H₂ reduction of WCl₆ in a hot wall vapour-plating process at atmospheric pressure. At temperatures below 450°C a coarse, porous, and noncoherent deposit was obtained resulting from incomplete reduction of the tungsten chloride. Between 550 and 650°C dense, coherent films were deposited. However, at temperatures above 700°C fine, particulate tungsten was formed by homogeneous reactions. These authors also observed that tungsten oxychlorides (WOCl₄ and WO₂Cl₂) caused formation of a highly porous, nonadherent deposit, thus showing the necessity of removing these contaminants from the WCl₆ source.

Tungsten CVD for integrated circuit metallization using WCl₆ was investigated by Melliar-Smith et al. [6]. Low-resistivity (6–15 μΩ-cm) films were obtained by H₂ reduction of WCl₆ at atmospheric pressure in the temperature range 550 to 950°C. The films showed excellent adhesion to silicon substrates. However, adhesion was poor at tem-

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temperatures higher than 850°C due to silicide formation.

Härsta and Carlsson [7] reported the results of a thermodynamical and experimental investigation of tungsten CVD using WCl₆ as tungsten source. They showed that tungsten can be deposited selectively on silicon from H₂/WCl₆ mixtures in a hot wall reactor at WCl₆ and H₂ partial pressures of 0.12 and 2.4 Torr, respectively. The growth rates were low and reproducibility was poor in the temperature range 475 to 750°C.

In the present work CVD of tungsten from WCl₆ was investigated experimentally using a cold wall reactor at a considerably higher H₂ partial pressure of 40 Torr and at atmospheric pressure. The films were characterized with respect to resistivity, morphology and impurity content.

2. Experimental

Tungsten films were deposited in a cold wall reactor with a resistively heated graphite susceptor. The CVD set-up was equipped with a quartz vessel serving as evaporation chamber for solid CVD precursor sources, in this case tungsten hexachloride. Nitrogen, purified by a copper catalyst (BASF Catalyst R 3-11), was used as purge and WCl₆ carrier gas. Hydrogen was purified by a palladium catalyst (BASF Catalyst R 0-20). WCl₆ (99.9%), obtained from Alfa Products, was purified by preliminary sublimation of tungsten oxychlorides WO₃Cl₂ and WOCl₄ at 100°C in a nitrogen flow. 15 × 15 mm sized silicon samples, cut from (100) oriented 10–15 Ω·cm p-type Si wafers, served as deposition substrates. The samples were cleaned in concentrated HNO₃ solution and received a 1 min 5% HF dip to remove native silicon oxide prior to deposition. Deposition experiments were also conducted on other substrate surfaces, i.e. 1 μm TiN on Si deposited by CVD, 24–27 nm W on Si produced by silicon reduction in the usual WF₆ process at 385°C, 155 and 2260 nm W on Si produced by hydrogen reduction of WF₆ at 435°C, and polished Mo samples. The substrate temperature, ranging from 480 to 670°C, was calibrated versus susceptor temperature for different experimental conditions (pressure, gas flow). WCl₆ was evaporated at temperatures ranging from 155 to 190°C in the depositions carried out at atmospheric pressure, and at 125 to 135°C in the experiments at 40 Torr pressure in a 1000 scem carrier (H₂ or N₂) gas flow. Film thickness was obtained from weight increase of the samples and from scanning electron microscopy (SEM) photographs of cross sections. X-ray diffraction was employed for identification of crystalline phases. The resistivity values of the films were measured using a four-point probe. Impurity contents of the deposited layers were determined by Auger electron spectroscopy (AES) and electron probe micro analysis (EPMA).

3. Results and discussion

3.1. Growth rate and morphology

Tungsten films deposited at atmospheric pressure on silicon substrates in the temperature range 525 to 625°C are non-uniform with rough surfaces as observed by SEM. Fig. 1 shows the characteristic type of surface obtained at evaporation temperatures of 155 to 170°C, corresponding to WCl₆ vapour pressures of 1.0–2.5 Torr. The growth rate is limited by gas-phase diffusion of the reactant (WCl₆) to the substrate surface. At WCl₆

Fig. 1. Scanning electron micrograph of a tungsten film surface showing diffusion-limited growth at atmospheric pressure.
evaporation temperatures of 180 to 190°C, corresponding to vapour pressures of 4 to 7 Torr, tungsten particle formation is observed (fig. 2) indicating nucleation of tungsten in the gas phase. Growth rates are found to be 70–200 nm/min. These values are averages obtained from SEM cross sections.

At a pressure of 40 Torr smooth films were obtained in the temperature range 480–670°C at WCl₆ evaporation temperatures of 125 to 135°C (vapour pressures 0.15–0.30 Torr). Fig. 3 shows a cross section of a film deposited at 625°C. At this pressure the growth rate is controlled by surface reactions. Fig. 4 shows growth rates as a function of reciprocal deposition temperature of films deposited at 40 Torr. The rates are significantly higher than those obtained by Härsta and Carlsson [7] in their hot wall reactor experiments. The higher deposition rate may be due to the higher H₂ pressure used in this work, assuming that the deposition rate increases with increasing H₂ partial pressure as in the WF₆/H₂ process, in which an order of one half in H₂ partial pressure was found [8,9]. In the atmospheric pressure CVD experiments of Melliar-Smith et al. [6] the highest growth rate using a WCl₆/H₂ mixture was 100 nm/min at 750°C in the gas-phase diffusion-limited regime.

Fig. 3. Scanning electron micrograph of a cross section of a tungsten film deposited at 40 Torr.

Fig. 4. Growth rate as a function of reciprocal substrate temperature for film deposition on Si at 40 Torr.
In comparison with the WF₆/H₂ process in this temperature range the growth rates of the WCl₆/H₂ process are low.

3.2. Reproducibility

Fig. 4 shows a considerable variation in growth rate of films deposited under identical experimental conditions indicating poor reproducibility of the process. Härsta and Carlsson [7] attributed the lack of reproducibility of the WCl₆/H₂ process to the presence of native silicon oxide on the silicon surface. Nucleation of tungsten is very sensitive to native silicon oxide preventing Si reduction of WCl₆ as first step in tungsten CVD. Although the removal of SiO₂ by WCl₆ producing WO₂Cl₂ is thermodynamically favourable, the reaction is subject to kinetic limitations. According to Busta and Tang [10] the WF₆-based process does not suffer from nucleation and reproducibility problems at native-oxide thicknesses less than 10 Å. WF₆ has a better ability to etch native silicon oxide than WCl₆.

3.3. Film structure and analysis

X-ray diffraction patterns show the formation of polycrystalline α-W on silicon substrates at atmospheric pressure. No evidence for the presence of silicide phases (WSi₁₂ or W₂Si₃) was found. In a few films a small amount of β-W was detected.

Layers produced at 40 Torr consist of α-W and again no silicide formation was observed. One film deposited at 490°C contained β-W.

The average oxygen content of the α-W films deposited at 40 Torr was less than 1% as indicated by EPMA and Auger measurements, and using EPMA no carbon or chlorine was detected. In the films containing β-W more than 1% oxygen was found. The formation of β-W indicates the presence of relatively high concentrations of oxygen in the reactor system or tungsten precursor.

3.4. Resistivity

The resistivity values of the films deposited at atmospheric pressure cannot be determined accurately because of non-uniformity of the films. Resistivities of the films deposited at 40 Torr are plotted versus film thickness in fig. 5. The values range from 7.9 to 17 μΩ·cm in the film thickness range 100 to 800 nm. These values are comparable to those reported by Melliar-Smith et al. [6] and values obtained in the conventional WF₆/H₂ process [3]. The bulk resistivity of α-W is 5.3 μΩ·cm. The film containing β-W has a considerably higher resistivity value of 41 μΩ·cm, in agreement with results of Tang and Hess [11] who found 40 μΩ·cm for β-W films deposited by plasma enhanced CVD.

3.5. Film adhesion

After exposure to the atmosphere for several days a few layers showed loss of adhesion, apparent from bubble formation as is shown in fig. 6. The lack of adhesion may be due to the formation of a gaseous product at the W/Si interface involving chlorinated species.
3.6. Other substrate materials

Tungsten film deposition on W/Si substrates resulted in growth rates of 8 nm/min at 540 °C and 50 to 67 nm/min at 624 °C. These growth rates are comparable to growth rates reported for silicon substrates. At 624 °C formation of WSi₂ occurred as revealed by XRD. This indicates that the films deposited using the regular WF₆ process at relatively low temperatures reacted with the Si substrate during the subsequent WCl₆ process at higher temperature. This observation suggests that the concentration of oxygen at the W/Si interface is lower in the films produced from WF₆/H₂ than in the films produced from WCl₆/H₂, since Pauleau et al. [12] have shown that silicide formation can be prevented by oxygen at the W/Si interface. They found that the silicide formation reaction starts at 625 °C at interfaces with low oxygen concentrations and is inhibited below 800 °C by higher oxygen concentrations. Hashimoto and Koga [13] deposited WSi₂ containing tungsten films from WCl₆/H₂ at temperatures higher than 1000 °C. The absence of interfacial W–Si reactions during tungsten deposition on Si from WCl₆ even at 670 °C in our work is consistent with the assumption that WCl₆ is unable to remove native silicon oxide under these conditions. Hence oxygen remains at the W/Si interface. An increased oxygen concentration at the interface could not be evidenced by AES depth profile measurements.

On Mo and TiN surfaces growth rates were found to be 6 to 10 nm/min at 540 °C and 40 nm/min at 624 °C.

In the absence of hydrogen, i.e., using a N₂/WCl₆ mixture, a decrease of tungsten film thickness of W/Si substrates was observed due to etching by WCl₆. Thermodynamical calculations, using a modified version of the program SOLGASMIX [14], predict the formation of tungsten subchlorides WCl₂ and WCl₄ under these conditions. In the same experiments quartz substrates proved to be inert to WCl₆, thus confirming the assumption that the WCl₆–SiO₂ reaction is relatively slow at these temperatures.

4. Conclusions

Tungsten films have been deposited on Si by H₂ reduction of WCl₆ in a cold wall reactor at atmospheric pressure and at a pressure of 40 Torr in the temperature range 480–670 °C. Deposition at atmospheric pressure produces rough and non-uniform films indicating limitation by gas-phase transport of reactants to the substrate surface. At 40 Torr smooth films are obtained in the surface-reaction-limited regime. The growth rate is low compared to that in the WF₆/H₂ process. The film resistivities are comparable to those obtained in the WF₆ process. The reproducibility of the process is poor as the process is sensitive to the presence of native silicon oxide on the substrate surface.

The high deposition temperature and lack of reproducibility may be disadvantages in application of the WCl₆-based tungsten CVD process. However, further investigations are required to determine the suitability of WCl₆ as a precursor in metallization of integrated circuits.
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