

Growth characteristics and electrical resistivity of chemical vapor-deposited tungsten film

I-Shun Chang*, Min-Hsiung Hon

Department of Materials Science and Engineering, National Cheng Kung University, P.O. Box 32, Tainan, Taiwan

Received 26 January 1998; accepted 24 April 1998

Abstract

The chemical vapor-deposited (CVD) tungsten films using H_2/WF_6 chemistry were studied. A wide range of deposition temperatures and gas compositions was changed to investigate the boundary separating mass transport-controlled and surface reaction-controlled regimes, in which the latter is preferred to get the optimum properties of films. The experimental results show that with increasing WF_6 and/or decreasing H_2 concentrations the surface reaction-controlled region is expanded toward high temperatures, which can be explained by the different order dependence of deposition rate with respect to H_2 and WF_6 concentrations. The grain size of the tungsten films is not sensitive to deposition temperature of 370–610°C, while is larger for films deposited at higher WF_6 concentrations in hydrogen-rich atmospheres. Electrical resistivity of films of about 0.5 μm thickness was measured by four-point probe. Low film resistivity of 8.1–14.7 $\mu\Omega cm$ was obtained as deposited over a wide range of H_2/WF_6 ratio between 5 and 40 at 490°C and $2.7 \times 10^4 Pa$ (200 Torr). Larger electrical resistivity was obtained for the films deposited either by extra high H_2/WF_6 ratio or low ratio near 3, in which the former is attributed to the small grain size effect, while the latter is possible due to the fluorine incorporated into the film during deposition. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Chemical vapor deposition; Hydrogen; Tungsten; Tungsten hexafluoride

1. Introduction

Chemical vapor-deposited tungsten has been utilized in very large scale integrated (VLSI) structures due to its unique properties of low resistivity compared to polycrystalline silicon, high resistance to electromigration compared to aluminum, thermal stability, conformity of deposition and the ability of selective deposition. Among the applications for tungsten is as a diffusion barrier between silicon contacts and aluminum metallization to prevent aluminum spike-induced failures [1,2], recently as a conducting material to fill contacts or vias with high aspect ratio for higher density and advanced performance in integrated circuits [3–5]. Conformal step-coverage of CVD tungsten for filling high aspect ratio contact holes without void formation then becomes a great concern for the multilevel interconnect technology. Related literature has reported that for conformal step coverage of blanket CVD tungsten deposition using H_2/WF_6 or SiH_4/WF_6 chemistry, lower deposition temperatures, lower hydrogen (H_2) or silane (SiH_4) reactant concentrations and higher tungsten hexafluoride (WF_6)

concentrations [6–8] are the processing parameters preferentially selected.

Minimization of CVD tungsten film resistivity is also highly desirable, and since actively studied, it has been known that this resistivity decreases with increasing film thickness [9–11] and deposition temperature [12]. Impurities, especially oxygen and fluorine, distributed mainly around the grain boundaries or at the interface between tungsten and its underlayer (Si wafer or other glue layer), are considered the key factors for the increase in resistivity [13]. Small grain size is thought to be another factor for high resistivity because a thinner film is generally accompanied by a distribution of smaller grains in the film [11].

For a better conformal deposition, a surface reaction-controlled process is basically required. Either low deposition temperatures or high reactant concentrations in gas phase have been known to promise the surface reaction-controlled deposition. The present paper investigates how the composition of gas phase consisting of WF_6 , H_2 and Ar influences the change of transition temperature above which the deposition becomes mass transport-controlled instead of surface reaction-controlled. Resistivity is a function of the microstructure and purity of tungsten film, which is closely correlated with the deposition parameters. This paper also

* Corresponding author. Fax: +88 6623 80208;
e-mail: n5881107@sparc2.cc.ncku.edu.

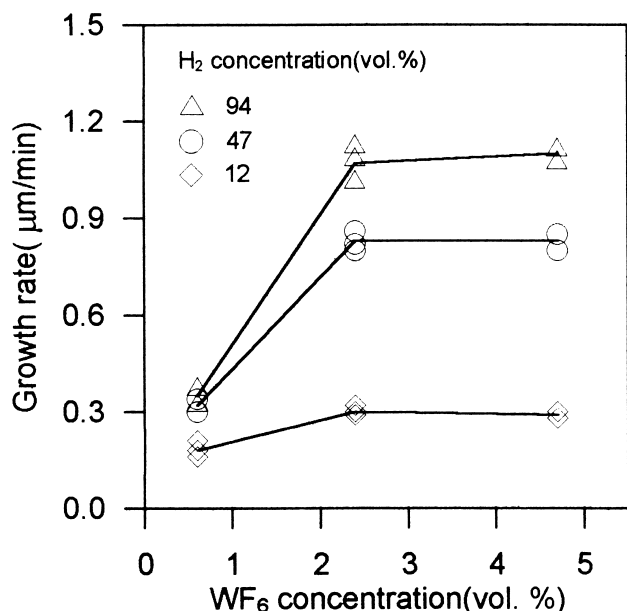


Fig. 1. The growth rate of tungsten films as a function of WF_6 concentrations. The other parameters are temperature 490°C , pressure 2.7×10^4 Pa, total flow 1700 sccm and Ar gas for balance.

discusses the interdependence of deposition parameters, microstructure and resistivity of the tungsten films.

2. Experimental procedures

A conventional tube-type (with 40 mm inner diameter) hot wall CVD reaction system was used to deposit tungsten film from $\text{H}_2/\text{WF}_6/\text{Ar}$ chemistry. The reactant gas was delivered into the reaction zone by a water-cooling pipe to attenuate the pre-consumption on the delivery way. The semiconductor grade of WF_6 was bought from AIR Products

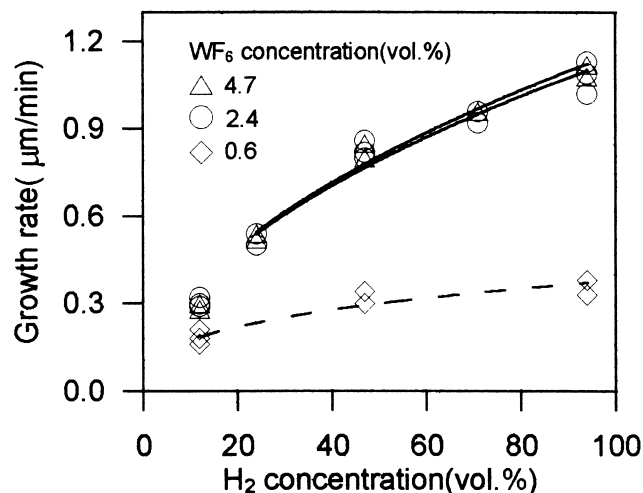


Fig. 2. The growth rate of tungsten films as a function of H_2 concentrations. The other parameters are temperature 490°C , pressure 2.7×10^4 Pa, total flow 1700 sccm and Ar gas for balance.

and Chemicals Inc. The n-type (111) silicon wafers, cut into 13-mm square pieces, were used as substrates which were ultrasonically cleaned with acetone for 5 min, followed by a 3-min deionized water rinse and a nitrogen blow dry. The wafers were then etched in 1 vol.% hydrofluoric acid solution for 1 min to remove the native oxide. After a rinse by deionized water and acetone and blow dry by nitrogen gas in sequence, the wafers were loaded immediately into the chamber ready to grow the tungsten film. The chamber was evacuated and purged with hydrogen during heating to insure cleanness. The flow of WF_6 gas from 10 to 80 sccm (0.6–4.7 vol.%), and H_2 gas from 200 to 1600 sccm (12–94 vol.%) were used to keep the ratios of H_2/WF_6 selected covering a wide range from sub- to super-stoichiometry of the reaction: $\text{WF}_6 + 3\text{H}_2 \rightleftharpoons \text{W} + 6\text{HF}$ (reaction 1). The deposition temperatures covered the range from 370 to 610°C . The flow rate for gases was 1700 sccm at a pressure of 2.7×10^4 Pa by adding Ar gas to keep the total gas flow rate constant. After deposition, the system was pumped continuously and allowed to cool in reduction atmosphere to approximate 100°C , below which point the samples were taken out.

The surface morphology and cross-section of the films were observed by SEM. Growth rate was obtained by thickness (measurement from SEM) divided by deposition time. The structure of film was characterized by XRD. Resistivity was determined by the thickness multiplied by the sheet resistance, measured by four-point probe.

3. Results and discussion

The dependence of the tungsten growth rate on the concentration of WF_6 is shown in Fig. 1, in which the growth rate at first increases significantly with increasing WF_6 concentrations from 0.6 to 2.4 vol.% for the two cases of higher H_2 concentrations. Increasing the WF_6 concentration further from 2.4 to 4.7 vol.%, however, does nearly not promote the growth rate any more. The saturated deposition rate with the WF_6 concentration from 2.4 to 4.7 vol.% indicates that the W-containing species (WF_x) have occupied almost all the active adsorption sites on the growing surface so that a larger amount of WF_6 input can even increase neither the reaction rate on the growing surface nor, as a result, the deposition rate. With a low H_2 concentration (12 vol.%), the growth rate decays slightly as the WF_6 concentration is higher than 2.4 vol.%. Similar phenomena have been reported [14,15]. From Yarmoff et al.'s [16] study, the dissociative chemisorption of WF_6 on Si(111) was found to be complete, but this reaction, however, is self-poisoning because the fluorine liberated from WF_6 (WF_x) will tie up the active Si sites responsible for the dissociation. Similar behavior is thought to have occurred in our experiments. Excess W-containing species and fluorine adsorbed on the growing surface would limit the reaction of dissociative adsorption of the arriving hydrogen, and the deposition

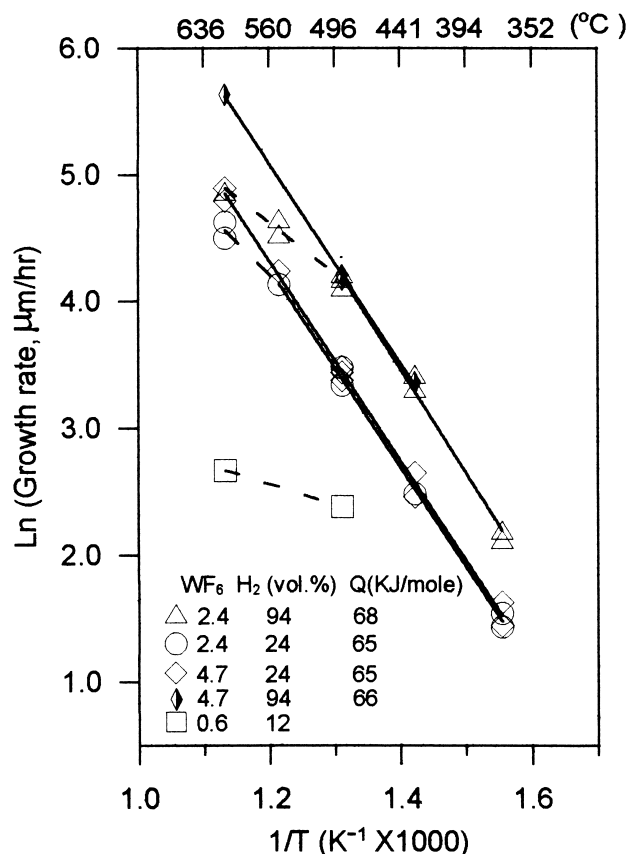


Fig. 3. Temperature dependence of tungsten deposition rate for various gas compositions. The other parameters are pressure 2.7×10^4 Pa, total flow 1700 sccm and Ar gas for balance.

rate was then decreased. Increase in the flux of hydrogen arriving at the growing surface will increase the possibility to form HF and then to desorb the occupied sites, and the self-poisoning effect is finally eliminated. As shown in Fig. 1, the decreasing growth rate with the increasing WF₆ concentration from 2.4 to 4.7 vol.% is not observed for higher H₂ concentrations.

Growth rate as a function of H₂ concentration is shown in Fig. 2. Each line represents the result of curve fitting through the experimental data points according to the power law. The two points are not taken into account while curve fitting is based on the happening of the self-poisoning effect mentioned above. For the median (2.4 vol.%) and the high (4.7 vol.%) WF₆ concentrations, the order of power-fitting lines is both about 0.5 with correlation coefficients about 0.98, while for the low WF₆ concentration of 0.6 vol.% the order is about 0.3 with worse correlation. The deposition rate of tungsten film with no measurable dependence on the WF₆ concentration and one-half order dependence on the H₂ concentration has been reported for a surface reaction-controlled deposition process with H₂/WF₆ chemistry [17–20]. The data for the low WF₆ concentration (0.6 vol.%) are thought to have been significantly influenced by mass transport.

In Fig. 3 the deposition rate of tungsten film was plotted as a function of temperature in an Arrhenius plot. The slopes for the solid lines are responsible for the apparent activation energy of values between 65 and 68 KJ/mole, close to 67 ± 3 KJ/mole usually given for the activation energy of the surface kinetically limited CVD-W deposition by H₂/WF₆ chemistry [17–21]. However, dashed lines in Fig. 3 exhibit the slopes of much lower values depending significantly on the deposition conditions. The extent of mass transport control becomes dominant in these dashed-line regions. Most attention is paid to the change of transition temperature, above which the onset of significant mass transport control is obvious. Depending on the H₂/WF₆ (volume percent ratio), the transition temperature is about 490°C with 94:2.4, 610°C with 94:4.7, 550°C with 24:2.4, and 610°C with 24:4.7. It follows that the increase of the WF₆ concentration in the gas phase will extend the surface reaction-controlled region toward higher temperatures, but in contrast the increase of H₂ concentration will expand the mass transport-controlled region toward lower temperatures. This can be understood based on the order of deposition reaction with respect to WF₆ and H₂, respectively. It has been well known that in the surface reaction-controlled region the reaction rate of the hydrogen reduction of tungsten hexafluoride reaction is of the order of 0.5 with respect to the hydrogen concentration, and of the order of zero or 1/6 with respect to the concentration of WF₆ [17–21]. When the deposition is originally carried out in the surface reaction-controlled region, further increasing the bulk H₂ concentration (correspondingly increasing the flux of hydrogen arriving at the growing surface) will speed up the reaction of tungsten formation. Although the increasing hydrogen-rich gas phase would promote also the diffusion flux of WF₆ from the bulk stream to the growing surface [22], the growing surface becomes finally W-containing species starved due to the limited WF₆ supply from the bulk stream. Once the WF₆ concentration gradient forms in the close front of the growing layer, the rate of WF₆ transport from the bulk stream to the growing layer dominates the deposition rate of tungsten film. On the opposite side, however, for the zero order of the WF₆ concentration on the deposition rate, the excess flow of WF₆ in the gas phase will not even stimulate the surface reactions on the growing layer when the film is deposited in the surface reaction-controlled region. But a larger flow of WF₆ involves a larger diffusion flux of WF₆ to the growing layer, which affords the WF₆ needed by the more active surface reactions proceeding on the growing layer at higher deposition temperatures. So the surface reaction-controlled region in Fig. 3 is extended to higher temperatures.

CVD processes have been well known to be usually surface reaction-controlled at low temperature, high reactant concentration and flow rate of gas; on the opposite side, they are mass transport-controlled [23–25]. Lower total pressures are also preferred to reaction-controlled process [26]. So the blanket tungsten deposition has commonly been

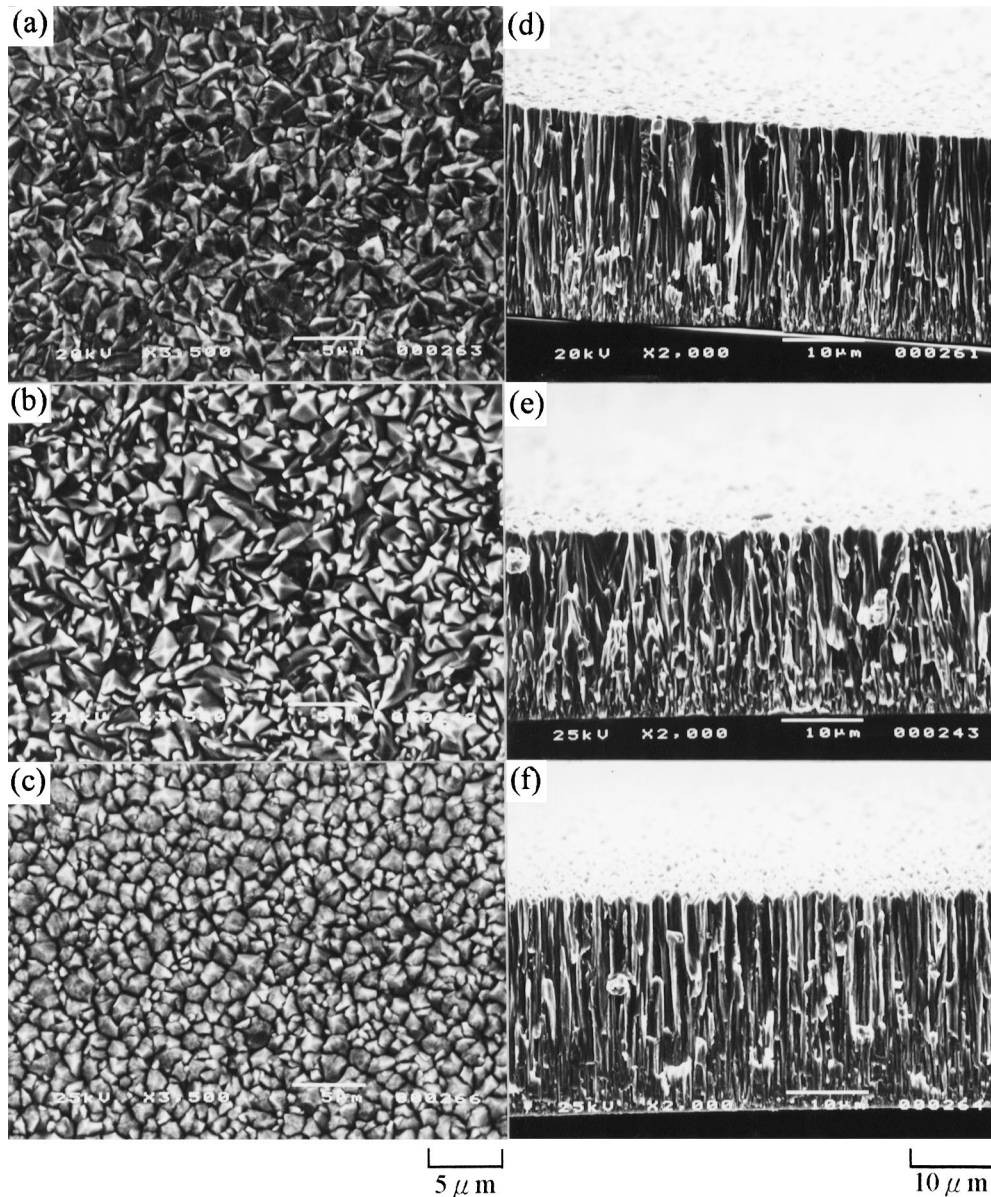


Fig. 4. The surface morphology and cross-section of tungsten films of about 24 μm obtained at temperatures of (a) 370°C, (b) 490°C and (c) 610°C. The other parameters are H_2 concentration of 94 vol.%, WF_6 concentration 2.4 vol.%, pressure 2.7×10^4 Pa, total flow 1700 sccm and Ar gas for balance.

conducted at low deposition temperatures and/or low system pressures to achieve the conformal CVD-W deposition [3,6]. With the H_2/WF_6 chemistry, either a higher WF_6 partial pressure or a lower H_2 partial pressure has also been shown as a key factor for the conformal deposition of tungsten film [6,7,27]. From the present study, it is known that a higher WF_6 or lower H_2 partial pressure in practice promises the surface reaction-controlled processes.

Fig. 4 shows SEM micrographs of the surface morphology and the cross-sectional view for films obtained at 94:2.4 H_2/WF_6 chemistry at various deposition temperatures. The films are 24 μm in thickness. As seen in the micrographs, the grains are more faceted for films deposited at higher deposition temperatures because the adatoms become more mobile on the growing layer with increasing temperatures.

The films all have well developed columnar grain structure. The surface of the film is rougher for the film deposited at 610°C, usually involving a diffusion-controlled deposition. The distribution of grain size seems insensitive to deposition temperatures considered here, similar to the published results [9,11]. In contrast, the morphology changes significantly when the gas composition is varied through a wide range during deposition. Fig. 5 shows some examples deposited with various gas composition at a temperature of 490°C, showing that the grain size of crystals spreads over a wide range. In a hydrogen-rich atmospheres (94 vol.% H_2), faceted crystals develop well with larger grains for higher WF_6 concentrations, as shown in Fig. 5a–c. Fig. 5a shows film obtained at the condition of the top H_2 (94 vol.%) together with the lower WF_6 concentration (0.6

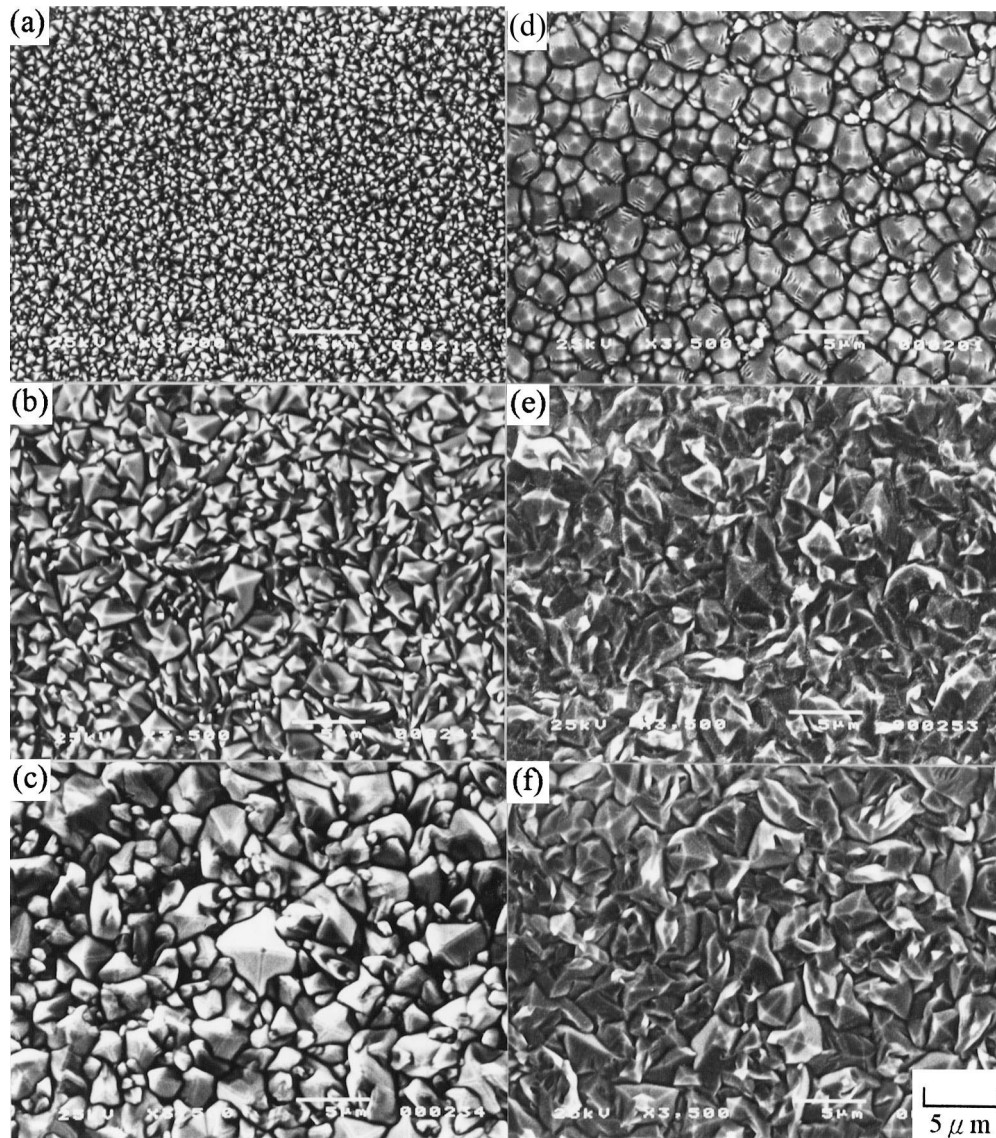


Fig. 5. The surface morphology of about 24- μm thick tungsten films obtained at various gas compositions. The volume ratio of H_2/WF_6 is (a) 94:0.6, (b) 94:2.4, (c) 94:4.7, (d) 12:0.6, (e) 12:2.4 and (f) 12:4.7. The other parameters are temperature 490°C, pressure 2.7×10^4 Pa, total flow 1700 sccm and Ar gas for balance.

vol.%), with a fine-grain feature. It is a result of a nucleation of high density in the beginning of growth in combination with a low-rate coalescence between adjacent crystals in the following growth. The crystal grains become larger with

Table 1

Resistivity ($\Omega \text{ cm}$) of 0.5- μm thick tungsten films deposited at various gas compositions. The other parameters are temperature 490°C, pressure 2.7×10^4 Pa, total flow of 1700 sccm and Ar gas for balance

WF_6 (vol.%)	H_2 (vol.%)	
	12	94
0.6	14.7 ± 1.6	17.4 ± 0.5
2.4	13.1 ± 0.4	9.7 ± 0.2
4.7	33.2 ± 0.8	8.1 ± 0.4

increasing WF_6 concentrations. With the H_2 -poor atmospheres (12 vol.%), no obvious difference of grain size was observed among the films for Fig. 5d–f. With increasing WF_6 concentration, unlike the cases for high H_2 concentrations where the growth rate increases significantly until the saturated growth rate, the growth rate of films deposited at such a low H_2 concentration at first increases only slightly and thereafter remains at a low rate or even decreases tenderly, as shown in Fig. 1. The deposition reaction in fact suffers from the mass transport of reactant from the gas stream, e.g. the transport of hydrogen to the growing layer for Fig. 5e,f. So the grain size of crystals was not changed significantly by increasing WF_6 supply, as shown in Fig. 5d–f.

Resistivity was measured for films of Fig. 5 but with 0.5 μm in thickness, and the results are shown in Table 1. With

high H_2 concentration of 94 vol.%, resistivity decreases with increasing WF_6 concentration: Resistivity is of 17.4, 9.7 and then 8.1 $\mu\Omega$ cm corresponding to WF_6 concentration of 0.6, 2.4 and 4.7 vol.%, respectively. This observation may be attributed to the grain-size effect, see Fig. 5a–c. For thin film of the same thickness, the smaller grain size will take the larger grain boundary area, and then will enlarge the grain-boundary scattering. A higher averaged concentration of oxygen impurity originating from the native oxide of silicon and from the ambient is charged usually by a finer-grain film, which is also thought to enhance the boundary-scattering significantly [11]. Opposite to the cases of high H_2 concentration, the largest film resistivity of about 33.2 $\mu\Omega$ cm was obtained at the top WF_6 concentration of 4.7 vol.% and at low H_2 concentration of 12 vol.%. This abrupt increase of resistivity for film obtained at the H_2/WF_6 ratio of 2.5, lower than the stoichiometry for reaction (1), is thought to be closely related to the large amount of incorporated fluorine during deposition due to the low concentration of H_2 relative to WF_6 .

4. Conclusion

It has been found that for CVD-W deposition, the transition temperature, above which the deposition rate is dominated by the mass transport control rather than by the surface reaction control, is affected significantly by the gas composition. The transition temperature is shifted to higher temperatures by increasing the WF_6 concentration; however, to lower temperatures by increasing the H_2 concentration. This can be understood by the order dependence on the deposition rate with respect to the individual reactant, where the order is one-half for H_2 and zero for WF_6 for the tungsten deposition dominated by the surface reaction control. The grain size of crystals of the film was found to be insensitive to the deposition temperatures considered here. However, the crystals are of larger sizes if deposited at higher WF_6 concentrations in hydrogen-rich atmospheres, which in turn leads to lower film resistivity, e.g. the lowest value of 8.1 $\mu\Omega$ cm for film of 0.5 μ m thickness was obtained at the condition of top WF_6 (4.7 vol.%) and H_2 concentration (94 vol.%) atmosphere at 490°C. The largest resistivity of 33.2 $\mu\Omega$ cm for film deposited under the $H_2/$

WF_6 ratio of 2.5 only, is thought to be the incorporated fluorine possibly with a larger amount during film deposition.

References

- [1] N.E. Miller, I. Beinglass, *Solid State Technol.* 25 (1982) 85.
- [2] M.L. Green, R.A. Levy, *J. Electrochem. Soc.* 132 (1985) 1243.
- [3] K.M. Chang, T.H. Yeh, S.W. Wang, C.H. Lee, *J. Electrochem. Soc.* 144 (1997) 996.
- [4] R.V. Joshi, V. Prasad, M.L. Yu, G. Scilla, *J. Appl. Phys.* 71 (1992) 1428.
- [5] W.K. Yeh, Y.C. Shiau, M.C. Chen, *J. Electrochem. Soc.* 144 (1997) 214.
- [6] S. Chatterjee, C.M. McConica, *J. Electrochem. Soc.* 137 (1990) 328.
- [7] A. Hasper, J. Holleman, J. Middelheek, C.R. Kleijn, J. Hoogendoorn, *J. Electrochem. Soc.* 138 (1991) 1728.
- [8] J.E.J. Schmitz, A. Hasper, *J. Electrochem. Soc.* 140 (1993) 2112.
- [9] C.M. Melliar-Smith, A.C. Adams, R.H. Kaiser, R.A. Kushner, *J. Electrochem. Soc.* 121 (1974) 298.
- [10] T.I. Kamins, D.R. Bradbury, T.R. Cass, S.S. Laderman, G.A. Reid, *J. Electrochem. Soc.* 133 (1986) 2555.
- [11] A.J. Learn, D.W. Forst, *J. Appl. Phys.* 58 (1985) 2001.
- [12] A.K. Sinha, T.E. Smith, T.T. Sheng, N.N. Axelrod, *J. Vac. Sci. Technol.* 10 (1973) 436.
- [13] S.-L. Zhang, R. Palmans, C.S. Petersson, K. Maex, *J. Appl. Phys.* 78 (1995) 7313.
- [14] K.J. Kuijlaars, C.R. Kleijn, H.E.A. van den Akker, *Thin Solid Films* 270 (1995) 456.
- [15] J.R. Creighton, in: V.V.S. Rana, R.V. Joshi, I. Ohdamari (Eds.), *Advanced Metallization for ULSI Application*, MRS, Pittsburgh, PA, 1992, p. 51.
- [16] J.A. Yarmoff, F.R. McFeely, *J. Appl. Phys.* 63 (1988) 5213.
- [17] W.A. Bryant, *J. Electrochem. Soc.* 125 (1978) 1534.
- [18] E.K. Broadbent, C.L. Ramiller, *J. Electrochem. Soc.* 131 (1984) 1427.
- [19] M.L. Hitchman, A.D. Jobson, L.F.T. Kwakman, *Appl. Surf. Sci.* 38 (1989) 312.
- [20] T.G.M. Oosterlaken, G.J. Leusink, G.C.A.M. Janssen, S. Radelaar, *J. Electrochem. Soc.* 143 (1996) 1668.
- [21] W.R. Holman, F.J. Huegel, *J. Vac. Sci. Technol.* 11 (1974) 701.
- [22] H.S. Choi, S.W. Rhee, *J. Electrochem. Soc.* 141 (1994) 475.
- [23] E. Sirtl, I.P. Hunt, D.H. Sawyer, *J. Electrochem. Soc.* 121 (1974) 919.
- [24] C.H.J. van den Brekel, *Philips Res. Repts.* 32 (1977) 118.
- [25] C.H.J. van den Brekel, *Philips Res. Repts.* 32 (1977) 134.
- [26] D.S. Rickerby, A. Matthews, *Advance Surface Coatings: A Handbook of Surface Engineering*, Chapman and Hall, New York, 1991, p. 180.
- [27] J.J. Hsieh, R.V. Joshi, in: V.V.S. Rana, R.V. Joshi, I. Ohdamari (Eds.), *Advanced Metallization for ULSI Application*, MRS, Pittsburgh, PA, 1992, p. 77.