

SOLID-STATE SCIENCE AND TECHNOLOGY

SiH₄-WF₆ Gas-Phase Nucleated Tungsten as an Adhesion Layer in Blanket Chemical Vapor Deposition for Ultralarge Scale Integration

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ABSTRACT

In this work, the thin tungsten film nucleated by an *in situ* SiH₄-WF₆ gas-phase reaction in the low pressure regime (100 mTorr) was investigated and used as an adhesion layer to replace TiN in a blanket chemical vapor deposition of tungsten (CVD-W) process. The deposition rate, step coverage, and film resistivity were studied as a function of the process parameters. Deposition rates from 360 to over 3000 nm/min were observed and increased with increasing deposition pressure and temperature. Moreover, we found that the deposition rate fell to zero when the temperature was less than 150°C. Also, the gas-phase reaction vanished when the SiH₄/WF₆ flow ratio was smaller than 1.6. On the other hand, the step coverage decreased with increasing deposition rate. Finally, the tungsten film resistivity was 167 μΩ-cm which was comparable to that of a sputtered TiN film (about 150 μΩ-cm) and also exhibited good adhesion ability on oxide when the temperature was higher than 200°C. Overall, the results indicate that this *in situ* gas-phase nucleated tungsten film is an attractive replacement for TiN film in the blanket CVD-W technique because of reduced process complexity, excellent step coverage, and low resistivity.

Introduction

Chemical vapor deposition of tungsten (CVD-W) has been attracting increasing attention as a conducting material to fill contacts or vias with high aspect ratio in ultralarge scale integration (ULSI) applications.¹⁻³ In a blanket CVD-W process, the need for an adhesion layer is usually considered to be a disadvantage of the process because of the poor adhesion of tungsten films on dielectrics. It is well known that TiN is the most promising candidate for a glue layer material in blanket CVD-W technology.⁴ TiN shows excellent adhesion on dielectrics such as silicon dioxide and silicon nitride as well as acting as a superior barrier against silicon diffusion in contacts. It can also eliminate the aluminum trifluoride pileup at the W/Al interface in the via filling process.⁵ In addition, another advantage of the use of existing TiN technology is that the contact resistance already has been characterized. Nevertheless, sputtered TiN also possesses some drawbacks including process complexity, high film resistivity, and the long initiation times characteristics of H₂-WF₆ chemistry.^{5,6} Furthermore, generally there will be a different etching rate between the tungsten film and adhesion layer of TiN. The adhesion layer at the sidewalls of contacts and vias is susceptible to a faster etching rate due to the localized stress⁷ and the disparate etching selectivity. The etching out of the adhesion layer on sidewall can cause microvoids between the tungsten film and oxide wall. These voids may form a reliability hazard.

In the present study, an *in situ* gas-phase nucleated tungsten film used as the adhesion layer to replace sputtered TiN in the blanket CVD-W process has been investigated. McInerney *et al.*⁸ have reported that the spontaneous gas-phase reaction occurs when the SiH₄/WF₆ ratio is above 1.0 and the nucleation rate strongly depends on pressure and carrier gases. In this work, a high SiH₄/WF₆

flow ratio condition (*i.e.*, 2.5) of the gas-phase nucleated tungsten differentiated it from the low ratio (less than 1) of the typical CVD-W process. It was observed that the step coverage depended on process pressure and the adhesion ability was related to deposition temperature. At the same time, the gas-phase nucleated tungsten can be reproducibly deposited without attacking the underlying materials, especially for contact filling (*i.e.*, silicon consumption issue). The deposition of a gas-phase nucleated tungsten layer was followed by a typical CVD-W process (flow ratio of SiH₄/WF₆ was less than 1) to achieve a thick tungsten film. Many two-step processes for W-CVD have been investigated by previous workers. Joshi *et al.*⁹⁻¹² employed a two-step process to deposit a blanket tungsten film on a Ti/TiN layer. The initial step was a brief reduction of WF₆ with SiH₄ to enhance the nucleation of tungsten on the TiN surface. The second step was a H₂ reduction process for depositing the bulk of the tungsten film. In addition, Higuchi *et al.*¹³⁻¹⁵ proposed a selective CVD-W process involving an initial Si reduction of WF₆ followed by SiH₄ reduction of WF₆. The characteristics of good adhesion, no damage to the Si surface, low contact resistance, and small growth difference in n⁺ and p⁺-Si underlayers could be obtained. However, an extra adhesion layer of TiN film was needed in the above studies of blanket CVD-W techniques. Thus gas-phase nucleated tungsten is considered an attractive replacement for TiN film to reduce process complexity and this two-step deposition of a blanket tungsten film can provide consistent results for contact and via fillings.

Experimental

All samples were fabricated on 6 in. (100) p-Si wafers with 15 to 25 Ω-cm nominal resistivity. The wafers were cleaned by a standard RCA cleaning process. A 1200 nm thickness of oxide was thermally grown at 1000°C on

wafers for contacts characterization. Another group of wafers for via characterization was prepared by a sputtered-deposition of 100 nm thick aluminum films on thermally oxidized silicon wafers. A 50 nm thick TiN film was also sputtered over the aluminum layer as the antireflection layer, in sequence, covered with a 1000 nm thick plasma-enhanced chemical vapor deposited (PECVD) oxide. Through sequential photolithography processes and pattern definition with fluorocarbon-based (*i.e.*, $\text{CF}_4/\text{CHF}_3/\text{O}_2$ plasma) reactive ion etching chemistry, a set of contact holes and vias with sizes ranging from $5 \times 5 \mu\text{m}$ to $0.3 \times 0.3 \mu\text{m}$ were obtained. The 50 nm thick TiN layer which would have increased the via resistance was removed during the reactive ion etching of via hole. Prior to CVD-W process, the wafers were treated with various precleanings. The contacts were dipped in diluted HF solution ($\text{HF}:\text{H}_2\text{O} = 1:50$) for 20 s to remove silicon native oxide and also the vias were cleaned with 20 s of immersion into hot concentrated HCl solution ($\text{HCl}:\text{H}_2\text{O} = 1:1$ at 50°C) to remove the native oxide on aluminum surface. After precleaning, all wafers were loaded into load-locked cold wall CVD-W system to deposit tungsten film.

The base pressure of the W-CVD chamber (ULVAC-ERA1000 system) was 10^{-6} Torr and the laminarized gas flow system was designed to greatly reduce reactor wall contamination. The deposition parameters of the gas-phase nucleated tungsten films were as follows: the substrate temperature varied from 200 to 450°C and the total gas pressure varied from 100 to 950 mTorr. The flow rates of SiH_4 and WF_6 were 12.5 and 5 sccm without carrier gas, respectively. On the other hand, the parameters of typical CVD-W process included 5 mTorr in pressure, $\text{SiH}_4/\text{WF}_6/\text{H}_2$ flow rate of 12.5/20/1000 sccm, and a substrate temperature of 350°C . With these conditions, a deposition rate of selective CVD-W film was 250 nm/min. For analysis, we have employed scanning electron microscope (SEM) to characterize the tungsten films morphology and deposition rates. The various impurities in tungsten film and a W/Al interface were investigated by secondary ion mass spectrometry (SIMS). The composition of tungsten film was analyzed by the Auger electron spectroscopy (AES). Furthermore, the crystalline phase of CVD-W film was examined by x-ray diffractometry (XRD) and the resistivity of tungsten film was calculated from TENCOR m-gapeTM 300 that is a contactless sheet resistance meter.

Results and Discussion

The beginning of CVD-W deposition on a particular material depends on the ability of this material either to reduce directly the tungsten hexafluoride species or to support the SiH_4 (or H_2) reduction of WF_6 . Typically, tungsten tends to nucleate much easier on semiconductors and conductors such as silicon, silicides, and metals than on dielectrics. Therefore, the surface reaction dominates the tungsten deposition mechanism, and this is the reason why an adhesion layer is indispensable in the blanket CVD-W process. However, the extra need for an adhesion layer in the blanket CVD-W technique is regarded as a disadvantage of the process. In this work, an *in situ* gas-phase nucleated tungsten film used as the adhesion layer in the blanket CVD-W process has been studied. It was observed that the gas-phase silane reduction preceded the Si reduction or Al reduction with WF_6 on material surface when the SiH_4/WF_6 flow ratio was over 1.6 even if the Si reduction and Al reduction take place preferentially to the silane reduction due to more negative free energy of reaction. Meanwhile, the WF_6 was completely consumed by a large amount of SiH_4 before arriving on wafer surface. Tungsten nucleated through gas-phase reaction and then deposited on every material, including the dielectrics. As a result, the gas-phase nucleated CVD-W film exhibited a blanket deposition characteristics.

Figure 1 demonstrates the SEM pictures of tungsten films grown under different SiH_4/WF_6 flow ratios. It is

clear that the tungsten film failed to deposit well when the SiH_4/WF_6 flow ratio was believed 1.6 (Fig. 1a). On the contrary, the process with high flow ratio of SiH_4/WF_6 (*i.e.*, 2.5) revealed an excellent deposition as shown in Fig. 1b. In addition, the SiH_4/WF_6 flow rate of 12.5/5 sccm for the typical CVD-W process in our study acquired a selective deposition of tungsten film. It was speculated that the gas-phase reaction strongly depended on the critical parameter of reactant gas flow ratio and the gas-phase nucleation vanished in the process with low SiH_4/WF_6 flow ratio. These were also consistent with the previous results of Ref. 8. The gas-phase nucleated W particle counts drastically decreased when the SiH_4/WF_6 flow ratio was smaller than 1.5. Also, the deposition rate of the gas-phase nucleated tungsten film was zero when the temperature was less than 150°C . Furthermore, the flow rates of SiH_4 and WF_6 played a minor role in the tungsten deposition mechanism. We found that the process with low gas flow rates (*i.e.*, the SiH_4/WF_6 flow rate reduced to 6/2.5 sccm but at the same SiH_4/WF_6 flow ratio) induced an insignificant discrepancy in deposition behaviors except for a decrease of deposition rate.

Table I exhibits the relationship between the tungsten deposition characteristics and operating pressure. The step coverage in Table I is defined as the ratio of the thickness of the tungsten film at the sidewall at half depth and the nominal tungsten film thickness. As shown in Fig. 2a, the process with higher deposition pressure acquired a higher deposition rate but poor step coverage. This was because the high deposition pressure induced the fast gas-phase reaction rate and then depleted the reactants before they arrived in contacts or vias. The deposition of tungsten film within contacts or vias was thus restrained and the step coverage decreased with increasing the deposition pressure. Accordingly, the process with 100 mTorr of deposition pressure (Fig. 2c) proved the most superior step cov-

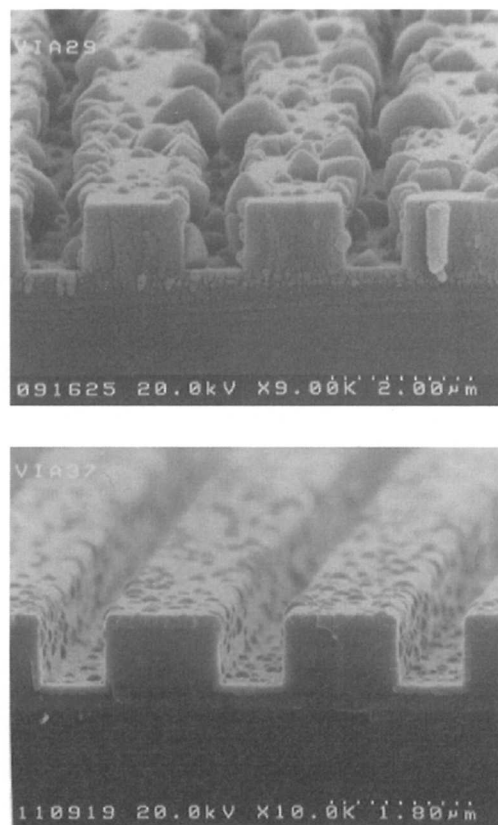


Fig. 1. SEM pictures of gas-phase nucleated tungsten films grown under various SiH_4/WF_6 flow ratios; (a, top) for SiH_4/WF_6 flow rate 12.5/8 sccm, and (b, bottom) for SiH_4/WF_6 flow rate 12.5/5 sccm. The deposition parameters are as follows: temperature = 350°C , pressure = 250 mTorr, and time = 10 s.

Table I. The deposition characteristics of W films with various deposition pressures.

Pressure (mTorr):	950	750	500	250	100
Deposited thickness, nm	Fig. 2a 692.3	423	Fig. 2b 276.9	Fig. 1b 173	Fig. 2c 78
Step coverage	≈ 0.39	≈ 0.5	≈ 0.75	≈ 0.85	≈ 1

The deposition recipes are as follows: SiH_4/WF_6 flow rate = 12.5/5 sccm, deposition temperature = 350°C, and time = 10 s.

erage. Figure 3 illustrates the via filling ability of the gas-phase nucleated tungsten film. The step coverage was 0.9 for an 80 nm thick gas-phase nucleated tungsten film deposited on the contact with an aspect ratio of 2.4 and a size of 0.5 μm . This value is better than that of the sputtered TiN.

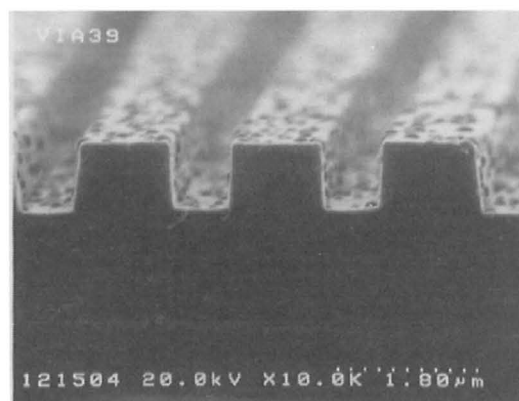
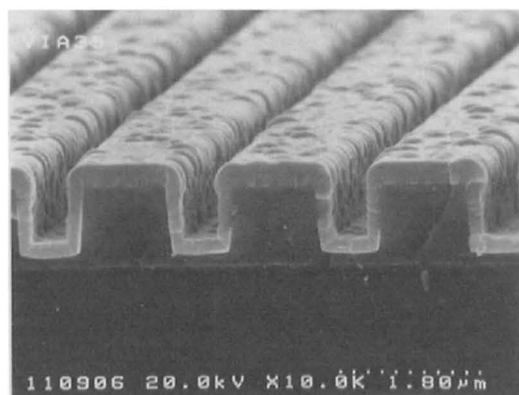
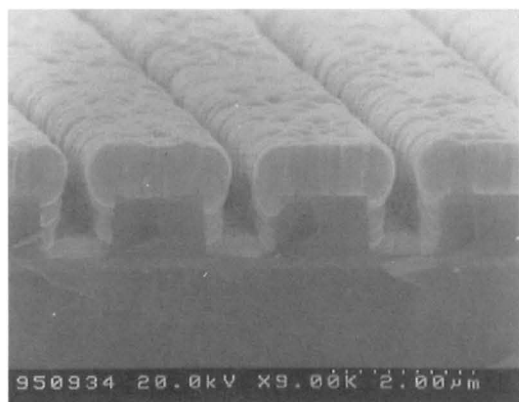


Fig. 2. SEM pictures of gas-phase nucleated tungsten films grown under various deposition pressures: (a, top) 950, (b, center) 500, and (c, bottom) 100 mTorr. The deposition recipes are as follows: SiH_4/WF_6 flow rate = 12.5/5 sccm, deposition temperature = 350°C, and time = 10 s.

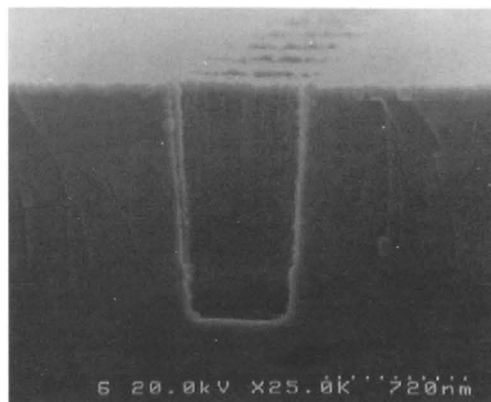


Fig. 3. Gas-phase nucleated tungsten film deposits on the contact with an aspect ratio of 2.4 and a size of 0.5 μm . The deposition recipes are as follows: SiH_4/WF_6 flow rate = 12.5/5 sccm, pressure = 100 mTorr, deposition temperature = 350°C, and time = 10 s.

Also, we have inspected the adhesion ability of the gas-phase nucleated tungsten film. It was found that the tungsten film started peeling off when the deposition temperature was less than 200°C. In addition, an indirect evidence by the stress measurement was obtained in Fig. 4 which revealed stress development upon annealing of three samples. For the case of sample A, typically chemical vapor deposition of tungsten in the regime where the surface reaction dominated and generally led to a well-defined dense structure. CVD-W process by SiH_4 or H_2 reduction with WF_6 on silicon substrate was always preceded by the Si reduction with WF_6 , which caused a tungsten interlayer with high growth stress (*i.e.*, 900 MPa in our work).¹⁶ The development of tungsten interlayer can be easily prevented by a thin inert SiO_2 layer.¹⁷ On the other hand, a lower temperature stress and slight change of stress between before and after annealing were examined in sample B. The gas-phase nucleated tungsten film could completely reduce the high stress level which occurred in the typical CVD-W. Also, the gas-phase nucleated W could act as a stress reliever. A prominent decrease of stress was found in the sample of a 300 nm thick typical CVD-W film stacked on a 70 nm thick gas-phase nucleated W (*i.e.*, sam-

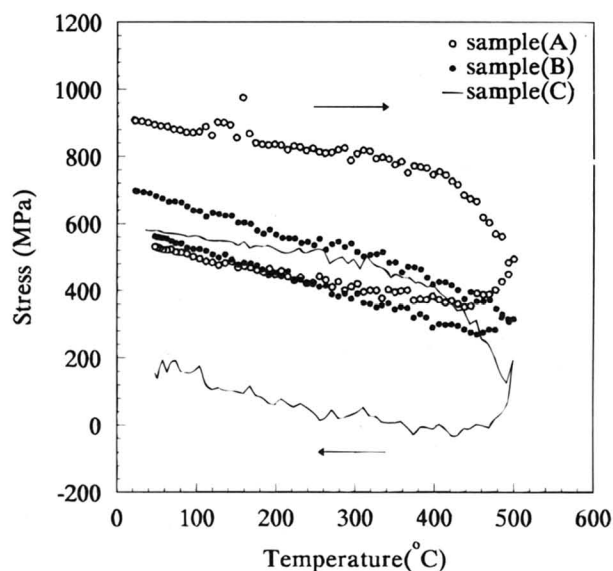


Fig. 4. Schematic representation of the stress behavior of three samples. Sample A for typical CVD-W (300 nm)/Si, sample B for gas-phase nucleated W (300 nm)/Si, and sample C for typical CVD-W (300 nm)/gas-phase nucleated W (70 nm)/Si structures.

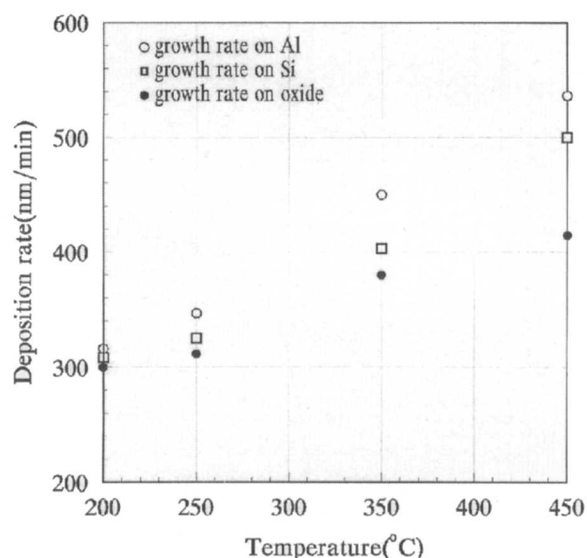


Fig. 5. The deposition rate of gas-phase nucleated tungsten on Si and Al surfaces at various temperatures. The deposition recipes are as follows: SiH_4/WF_6 flow rate = 12.5/5 sccm and pressure = 100 mTorr.

ple C). It is beneficial and important for the successful integration of tungsten in ULSI designs to investigate CVD-W deposition regimes which give low stress films.

As previous descriptions, the surface reaction played a negligible role in the deposition mechanism. Nevertheless, the surface reaction rate was promoted by increasing the deposition temperature and the influence of the surface reaction on deposition mechanism were also gradually considerable with increasing the temperature. Figure 5 expresses the deposition rates of tungsten films on PECVD oxide, silicon, and aluminum materials with various deposition temperatures. The deposition rates were measured by examining the tungsten film thickness on large-area silicon and aluminum surfaces (*i.e.*, not the regions within contacts and vias). We found that the difference of tungsten growth rate among these three materials increased with increasing the deposition temperature.

Furthermore, we have scrutinized the properties of two groups of tungsten films as listed in Table II. As shown in Fig. 6, the wafer of group A was fabricated with a two-step deposition process that consisted of a 50 nm thick gas phase nucleated tungsten film and a 400 nm thick typical CVD-W film. The wafer of group B included a 200 nm thick gas-phase nucleated tungsten film only. First, the morphologies of two groups of tungsten films were examined in Fig. 7. The gas-phase nucleated tungsten expressed a smoother but less crystalline surface. Moreover, the tungsten crystalline phases were also viewed. In the study of Schmitz *et al.*,¹⁸ a stable low resistivity α -W phase was obtained only for the flow ratios of SiH_4/WF_6 was smaller than 1.3. Between 1.5 and 3.8, a diffraction pattern could be identified with that of the *meta*-stable β -W phase or amorphous phase. These two phases manifested high tungsten film resistivity. According to the experimental

Typical CVD-W
Gas phase nucleated W
Oxide

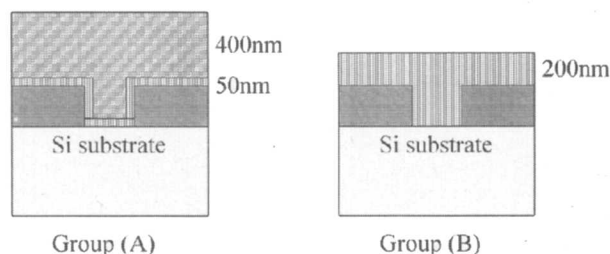
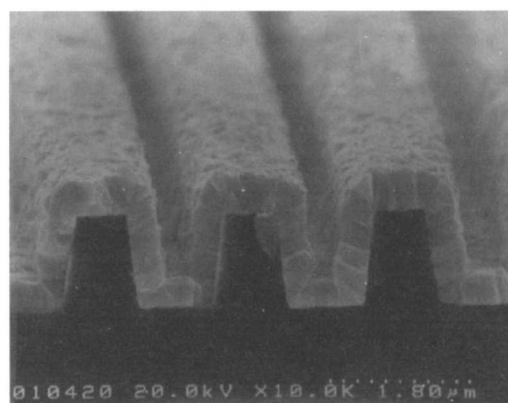


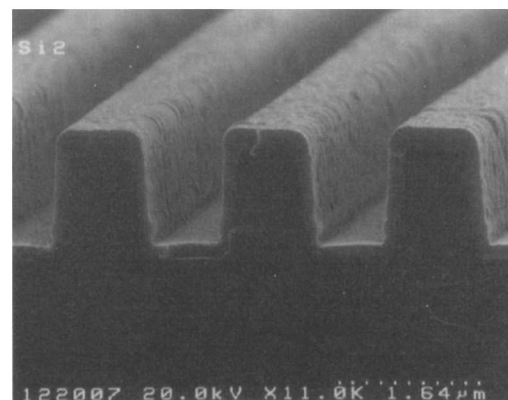
Fig. 6. Schematic diagrams of two groups of samples. Deposition recipe for the gas-phase nucleated tungsten is as follows: SiH_4/WF_6 flow rate = 12.5/5 sccm, temperature = 350°C, and pressure = 100 mTorr. Parameters for the typical W deposition include 5 mTorr in pressure, SiH_4/WF_6 flow rate of 12.5/20 sccm, and temperature of 350°C.

results of Fig. 8, the wafer of group A evidenced high intensity of the (110) α -W and (200) α -W peaks. On the other hand, the gas-phase nucleated tungsten film showed a broad amorphous (probably β -W) peak and without α -W phase detected.

More insight was obtained from the electrochemical film composition as indicated in Fig. 9. It is known that the β -W lattice is stabilized by impurities like fluorine¹⁹ or oxygen.²⁰ In our case the impurity is mainly silicon that



Group (A)



Group (B)

Fig. 7. The morphologies of two groups of tungsten films.

Table II. The various properties of W films of two groups. The wafer of group A consists of a 50 nm thick gas-phase nucleated tungsten film and a 400 nm thick typical CVD-W film on the silicon substrate. The wafer of group B involves a 200 nm thick gas-phase nucleated tungsten film only.

	Group A	Group B
W film morphology	Fig. 7a	Fig. 7b
W film crystalline phase	Fig. 8a	Fig. 8b
Film resistivity ($\mu\Omega\text{-cm}$)	23	167
Impurities distribution in W film (CVD-W/Al structure)	Fig. 9a	Fig. 9b

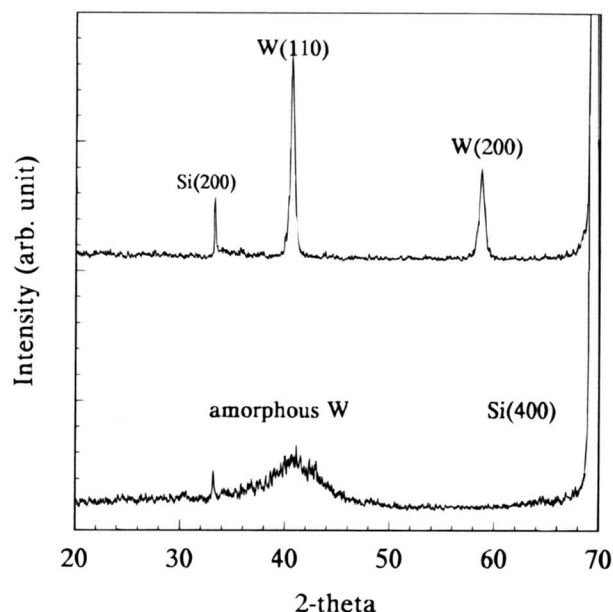


Fig. 8. The x-ray diffraction patterns of two groups of tungsten films.

caused the amorphous-W lattices. It is noted that the concentrations of oxygen of two groups of tungsten films were equivalent but the wafer of group B exhibited a higher Si and a lower F concentrations in tungsten film than those of the wafers of group A. This was because there was more SiH_4 presented that could be consumed by the WF_6 under the condition of high SiH_4/WF_6 flow ratio. The high Si content induced the high film resistivity as revealed in Table II. The gas-phase nucleated tungsten film had a resistivity of $167 \mu\Omega\text{-cm}$ that was larger than the $23 \mu\Omega\text{-cm}$ of the typical CVD-W film. However, the slightly high resistivity of the tungsten film in the application of adhesion layer is not a problem. In addition, the concentration of silicon in the gas-phase nucleated tungsten film was quantified by Auger electron spectroscopy (AES) analysis. The values of 55 and 41% were detected for the tungsten and silicon atomic concentrations, respectively, and the atomic ratio of silicon to tungsten approximated 0.75.

Another important phenomenon to be checked is the silicon consumption in contact filling. The silicon consumption provides valuable information about the quality of the CVD-W/Si interface and the leakage current of contacts. In most cases there will be a barrier material existing for contact reliability in blanket CVD-W technique, and this same barrier can be used as the adhesion layer. Since the gas-phase nucleated tungsten film is used as the adhesion layer in our study, the issues of silicon consumption and lateral encroachment are examined especially. It was observed that the deposition of the gas-phase nucleated tungsten was both reproducible and did not attack the silicon substrate. This result was inferred that a large amount of SiH_4 depleted the WF_6 before they arrived on the silicon surface. The probability of Si reduction with WF_6 was thus suppressed, and the problem of silicon consumption was also eliminated.

Finally, we have inspected the blanket CVD-W film for contact filling with a two-step deposition process as shown in Fig. 10. The parameters of the first step included 100 mTorr in pressure, SiH_4/WF_6 flow rates were 12.5/5 sccm, substrate temperature was 350°C , and the deposition times was 5 s. With these conditions, a 40 nm thick gas-phase nucleated tungsten film was obtained as the adhesion layer. The parameters of the second step (*i.e.*, typical CVD-W process) were as follows: substrate temperature was 350°C , total gas pressure was 100 mTorr; flow rates of SiH_4/WF_6 were 12.5/20 and 1000 sccm of H_2 as carrier gas.

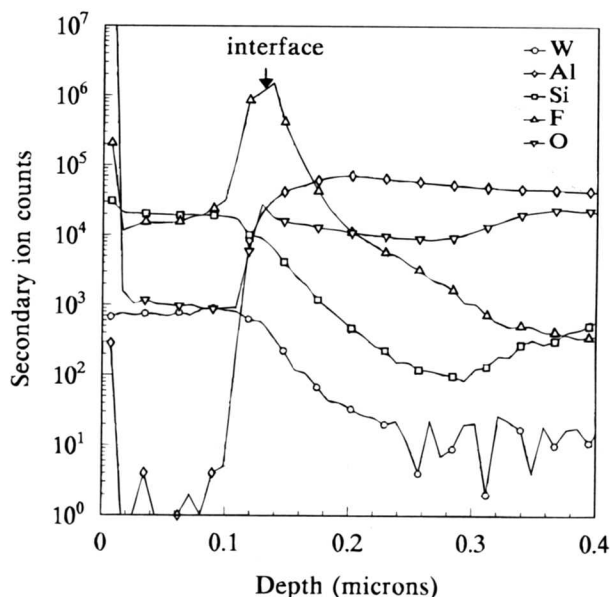
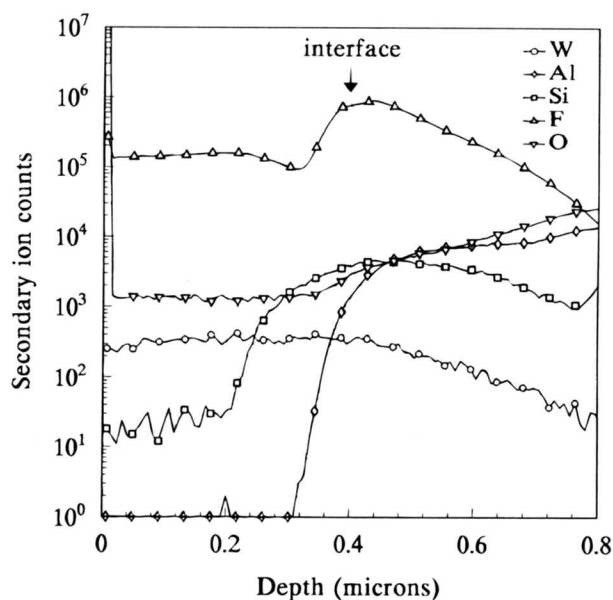


Fig. 9. The SIMS profiles of two groups of tungsten film deposit on aluminum material.

As shown this technique gives an excellent deposition of the blanket CVD-W film for the contact filling.

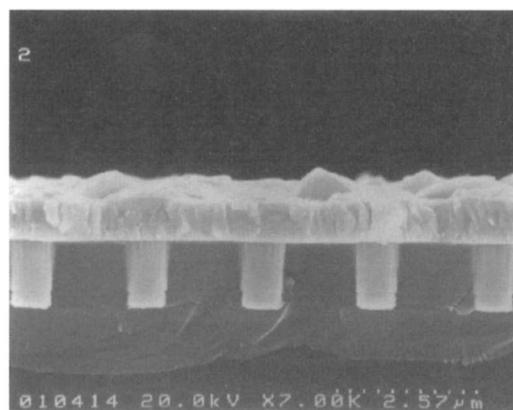


Fig. 10. The SEM picture of the blanket CVD-W film with a two-step deposition process for contact filling.

Summary

An *in situ* gas-phase nucleated tungsten film used as an adhesion layer in the blanket CVD-W process was investigated. The high SiH_4/WF_6 flow ratio condition (*i.e.*, 2.5) differentiated the gas-phase nucleated tungsten from the low ratio (less than 1) of the typical CVD-W process. The deposition rate increased with increasing deposition pressure and temperature. Also, the gas-phase reaction vanished when the SiH_4/WF_6 flow ratio was less than 1.6. The gas-phase nucleated tungsten film had a resistivity of $167 \mu\Omega\text{-cm}$ and exhibited good adhesive ability when the deposition temperature was higher than 200°C . Furthermore, a two-step deposition technique involving a thin gas-phase nucleated tungsten used as the adhesion layer and a following typical CVD-W process for achieving a thick tungsten film was developed. This two-step deposition technique has proved to provide a superior deposition for the blanket CVD-W process.

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