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Preparation of tungsten metal film by spin coating method

Hak-Ju Kim, Jung-Ho Lee[1], Il-Hyun Sohn[1], Tae-Jin Hwang[1] and Kwan-Young Lee*
Department of Chemical and Biological Engineering
Applied Rheology Center, Korea University, Seoul 136-701, Korea
[1]Samsung Electronics, Kiheung 449-712, Korea

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Abstract

Metal thin films, which are indispensable constituents of ULSI (Ultra Large Scale Integration) circuits, have been fabricated by physical or chemical methods. However, these methods have a drawback of using expensive high vacuum instruments. In this work, the fabrication of tungsten metal film by spin coating was investigated. First of all, inorganic peroxopolytungstic acid (W-IPA) powder, which is soluble in water, was prepared by dissolving metal tungsten in hydrogen peroxide and by evaporating residual solvent. Then, the solution of W-IPA was mixed with organic solvent, which was spin-coated on wafers. And then, tungsten metal films were obtained after reduction procedure. By selecting an appropriate organic solvent and irradiating UV, the sheet resistance of the tungsten metal film could be remarkably reduced.

Keywords : spin coating, tungsten, metal film, sheet resistance, isopolyacid, reduction, hydrogen peroxide

1. Introduction

Semiconductor devices in ultra large scale integration circuits are composed of various multi-layers. So, it is necessary to make thin films of dielectric, semi-conductive, and conductive substances. Metallization is a process of making thin films of conductive materials used for electrical contacts, interconnections between devices, and bonding external circuits with chips. With the large demand of ultra scale integration circuits, the importance of metallization has been much taken into account for the enhancement of process yield and reliability. For development of high yield metallization process, low surface resistance, ease of fabrication, mechanical and chemical stability and finally surface uniformity are required. At the early years, thermally stable metals like platinum and titanium, which had high electrical conductivity, were used as metal substances for semiconductor device fabrication processes. Then, aluminum was adopted for its advantages of physical properties and prices. However, since aluminum was easily oxidized to Al_2O_3 forming non-conductive layer in the presence of air, high vacuum (5×10^{-5} torr) system was required for the aluminum film processing, which caused the process cost to increase (Middleman, 1993; Lee, 1990; George, 1992).

In comparison to aluminum, tungsten had high electrical conductivity, low ohmic contact resistance and reliable patterning properties. So, it was used for contact layer, diffusion barrier, gate electrode and interconnecting line in ultra large scale integration technology. In 1855, Friedrich Whöhler firstly performed tungsten coating experiments using hydrogen and WCl_6. Then, in the 1960s tungsten film was used as an interconnection material of silicon device, which was fabricated by physical or chemical method. However, since highly toxic and explosive gases such as AsH_3, SiH_4 were used in large quantities in the conventional film coating processes like chemical vapor deposition (CVD), expensive high vacuum system was demanded for safe treatments.

Spin coating method is an easy and general process for coating polymer material or photoresist on silicon wafers. After dropping the coating solution onto the wafer, the degree of coating is controlled by the centrifugal force derived from the rotation perpendicular to the wafer. At low rotation speed, the coating solution spreads out on the wafer, and at high rotation speed (generally 2,000 ~ 4,000 rpm) thin films are formed. As described above, the spin coating method, distinctively compared to the conventional physical and chemical method, is a quite simple and effective way of making thin films with varying its thickness by just controlling parameters such as the time and speed of rotation as well as the viscosity and the density of the coating solution. But the spin coating method was thought not to be applicable to making metal films, because the precursors of the metals are difficult to be formed in liquid

*Corresponding author: kylee@korea.ac.kr
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state.

However, Okamoto and Ishikawa (1989) suggested a novel method of preparing metal films with spin coating method by dissolving tungsten metal powders in hydrogen peroxide. The resulting solution was dried to yield peroxopolytungstic acid powder. The powder can be dissolved in water and organic solvent solution, which could be applied to surfaces to form thin, crack-free inorganic peroxopolytungstic acid (W-IPA) films with an empirical formula of $WO_3 \cdot 0.65H_2O_2 \cdot 2.2H_2O$ (Okamoto *et al.*, 1989). The W-IPA films on Si wafers could be reduced in H_2 circumstances to produce metallic tungsten films. But the tungsten films prepared by the above method had a high sheet resistance owing to low density. As a result, further work on preparing tungsten metal films by spin coating method was not carried out.

In this work, by selecting the optimum organic solvent, we tried to prepare tungsten metal films having greater uniformity and density for higher electron transfer. And we investigated the effect of the irradiation of UV before the reduction procedure to make W-IPA films which have the enhanced uniformity and density due to the polymerization of the surface peroxopolytungstic compounds.

2. Experimental

2.1. Preparation of W-IPA powder

11.03 g of tungsten powder (99.9% pure, Aldrich) was slowly dissolved in 50 ml of 15% H_2O_2. After a brief induction period, a vigorous exothermic reaction occurred, which resulted in dissolving the tungsten powder to produce a clear yellow solution. 20 ml of 30% H_2O_2 was added in excess and the solution was kept for 3 hours. Unreacted tungsten powder was removed by filtration (0.1 μm filter paper). Then, the excess peroxide was decomposed by a fine platinum wire screen catalyst (99.9% pure, Aldrich). The resulting solution was dried at 35°C for 4 hours in rotary evaporator to yield the desired yellow W-IPA powder.

2.2. Preparation of W-IPA coating solution

In order to make a solution for spin coating, the prepared W-IPA powder was dissolved in de-ionized water to form 50 wt% solution. Here, organic solvents were added in order to increase the adhesion strength on oxidized Si wafers. The several kinds of organic solvents, such as N-methyl-2-pyrolidone, N,N-dimethyl formamide, 2-ethoyethanol, 2-methyl-2-propanol, 2-propanol, were investigated to obtain a high quality tungsten metal coated on Si wafer.

2.3. Measurement of the viscosity of the W-IPA coating solution

The kind as well as the amount of the added organic solvent also affects the viscosity of the W-IPA coating solution which is one of the main factors determining the film quality. To determine the optimum viscosity of the W-IPA coating solution, the viscosities of various W-IPA coating solutions having different concentration were measured with HAAKE viscometer (VT-501, HAAKE).

Table 1. Operational conditions of spin coater

Low Speed		High Speed	
Time (sec)	Spin Speed (rpm)	Time (sec)	Spin Speed (rpm)
0 ~ 5	500	5 ~ 40	2,500

2.4. Preparation of tungsten metal film

W-IPA solution was spin-coated on 4 in p-type oxidized Si wafer with a conventional spin coater. The conventional pre-treatment of the Si wafer with ammonium water and hydrofluoric acid had no influence on the surface morphology and structure of the film formed, so no wafer pretreatment was carried out afterwards. Process conditions of the spin coater are presented in Table 1.

The spin-coated wafer was cut into small fragments (1.5 cm×1.5 cm), which were reduced under pure H_2 (200 m*l*/min) at elevated temperatures. The only product of the reduction reaction was water and the unreacted H_2 was refluxed, while N_2 was used as a purging gas of the reduction reactor. The reactor was made of Pyrex tube of 4cm inside diameter and 40 cm length. The reduction temperatures were varied between 300~800°C for 30~120 minutes. The change of resistance due to the different reduction conditions was estimated. In order to increase the uniformity and density of tungsten film further, UV (30W, Sankyo Denki) was irradiated (2.9×10^{-3} J/cm^2·s) before the reduction procedure.

2.5. Characterization

The thickness and morphology of the prepared tungsten film were characterized by means of SEM (JSM-5310LV, JEOL) and the sheet resistance was measured by four point probe (Veeco FPP-5000). The structure of the tungsten film was analyzed by XRD (35 mA, 40 kV, CuKα X-ray, D/Max-3C, Rigaku).

3. Results and discussion

3.1. Optimization of the preparation procedure of W-IPA powder

During the preparation of peroxopolytungstic acid (W-IPA) by reacting tungsten metal powder with hydrogen peroxide, the degree of oxidation might be varied by the preparation procedures. It means that the amount of tungsten finally contained in the W-IPA powder might be varied. For higher tungsten density at film surface, larger

amount of tungsten in the W-IPA solution should be obtained. To confirm the exact amount of tungsten, the tungsten amount in the W-IPA solution was measured by varying the preparation procedures of the W-IPA powder. For the measurement of the amount of tungsten, methods suggested by Kudo (1987) were adopted. 5 g of W-IPA powders prepared by different procedures were heated to 700°C for 1 hour and baked for 2 hours, where metal tungsten could fully oxidized to tungsten oxide. And then, the amount of tungsten oxide was measured, which showed the amount of tungsten present in W-IPA powders. The preparation conditions and the change of weight of the W-IPA powders are presented in Table 2. The highest amount of tungsten was observed when 11.03 g of metal tungsten powder was dissolved in 50 m*l* of 15% hydrogen peroxide and 20 m*l* of 30% hydrogen peroxide was added in excess. The solubility of the W-IPA powders prepared by the different procedures was all high enough to make 50 wt% solution.

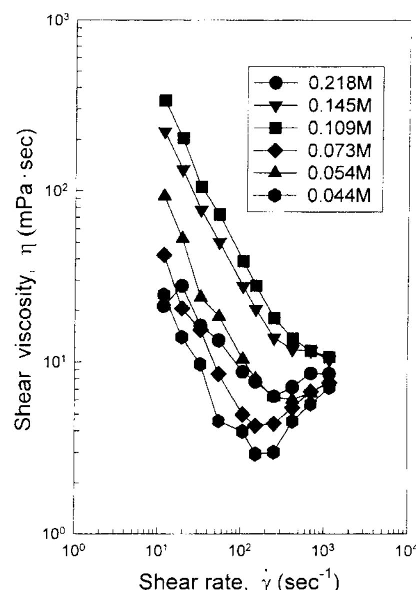


Fig. 1. Shear viscosity versus shear rate depending on concentration of W-IPA coating solution.

3.2. Optimization of the viscosity of the W-IPA coating solution

As shown in Fig. 1, 0.109 M of the W-IPA solution showed the highest viscosity in all shear rates. And regarding the uniformity and the density of the film formed, it was found to be the optimum viscosity. The W-IPA solution showed shear thinning behavior at all shear rates examined. Some solutions especially with low concentration showed shear thinning behavior at low shear rates below 100 sec^{-1}, while above that point they tended to show shear thickening behavior.

Table 2. Change of weight after calcinations (700°C, 2 h) in air for W-IPA powders obtained by different methods

Method	Weight (g)	Change of weight[a] (g)
Tungsten 4 g + 30% H_2O_2 50 m*l*	3.546	-1.454
Tungsten 4 g + 30% H_2O_2 25 m*l*	3.941	-1.059
Tungsten 4 g + 15% H_2O_2 25 m*l*	3.942	-1.058
Tungsten 4 g + 35% H_2O_2 25 m*l*	3.890	-1.110
Tungsten 11.03 g + 15% H_2O_2 50 m*l* + 30% H_2O_2 20 m*l*	4.219	-0.781

(a) Basis : W-IPA powder 5g

3.3. Selection of the organic solvent and properties of the tungsten films

Okamoto (1989) proposed that when 2-ethoxyethanol was added, adhesion strength could be increased between the wafer and the coating solution. The effects of organic solvents on the uniformity and density of the metal films were investigated by selecting a proper solvent considering their physical and chemical properties. For adequate adhesion and ease of decomposition by heating, the viscosity of the organic solvents should be in the range of 1~4 cP and the decomposition temperature should not be too high (Ishikawa, 1992). Selected organic solvents and their properties are given in Table 3. After the decomposition for 30 minutes at temperatures listed in Table 3, the uniformity and density of the resulting films were investigated by means of

Table 3. Physical properties of organic solvents and uniformity of films

Solvents	Molecular Weight	Viscosity @25°C (cP)	Boiling Point /Bakingpoint (°C)	Uniformity
N,N-Dimethyl formamide $HCON(CH_3)_2$	73.1	0.8	153 / 300	B
N-methyl-2-pyrrolidone C_5H_9NO	99.1	1.7	202 / 300	G
2-ethoxyethanol $HO(CH_2)_2C_2H_5$	90.1	2.1	136 / 300	C
2-methyl 2-propanol $(CH_3)_3COH$	74.1	4.3	82.4 / 150	C
2-propanol $(CH_3)_2CHOH$	60.1	2.0	82.3 / 150	B

G: good, B: bad, C: common

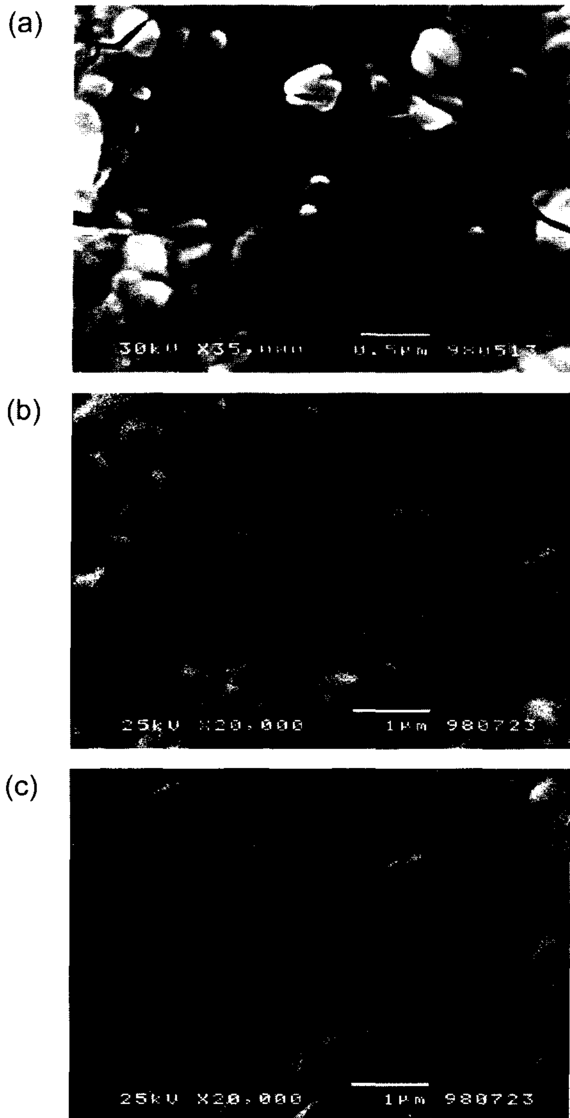


Fig. 2. SEM images of W-IPA films prepared (a) without organic solvent, (b) with 2-ethoxy ethanol, and (c) with N-methyl-2-pyrrolidone.

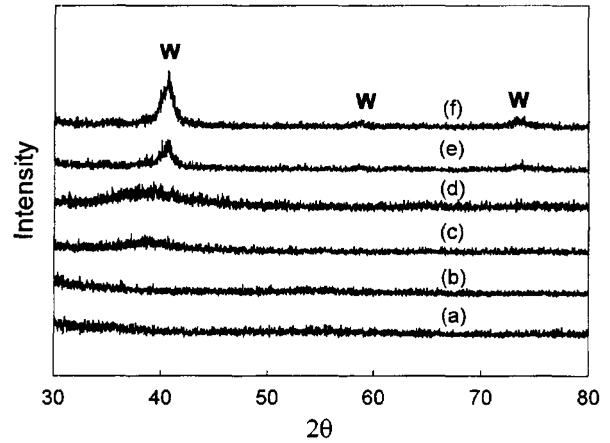


Fig. 3. XRD patterns of W metal film prepared at various reduction temperatures for 30 min.
(a) 300°C, (b) 400°C, (c) 500°C, (d) 600°C, (e) 700°C, (f) 800°C.

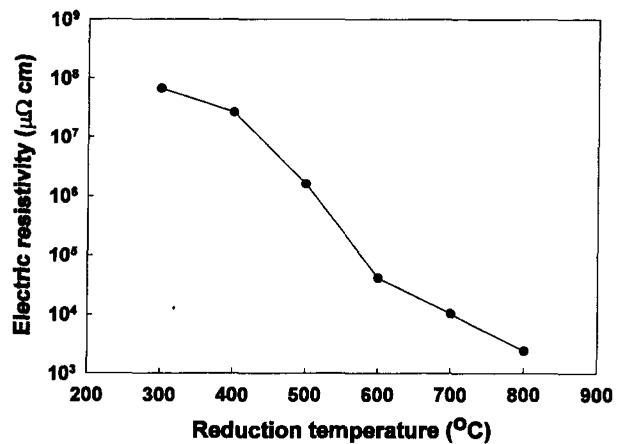


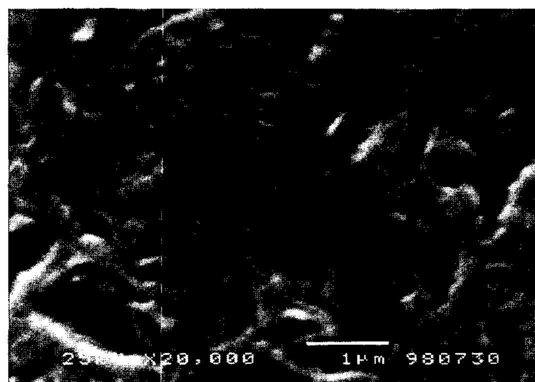
Fig. 4. Sheet resistance of W metal films prepared at various reduction temperatures.

SEM. From SEM images presented in Fig. 2, the film coated using N-methyl-2-pyrrolidone added solution showed the best uniformity and density.

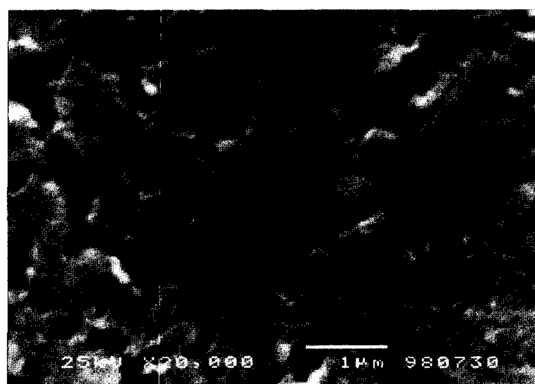
Electrical properties and structures of metal films after reducing the resulting films, which were prepared by the most effective organic solvent, N-methyl-2-pyrrolidone, were investigated by varying the reduction time and temperatures. First, reduction time was fixed to 30 minutes and the temperatures were varied from 300°C to 800°C. XRD patterns of the metal films prepared at these conditions were shown in Fig. 3. From 600°C, XRD peaks of metal tungsten appeared, which means that the soluble peroxotungstic substances were converted to insoluble tungsten oxides and finally reduced to tungsten metals above 600°C.

The sheet resistances of tungsten films reduced at different temperatures were measured by 4-point probe, which results are presented in Fig. 4. Sheet resistance tended to decrease as the reduction temperature increased, which was well matched to the facts explained by XRD. From SEM images of tungsten metal films reduced at 600°C and 800°C presented in Fig. 5, films reduced at higher temperature showed to have higher uniformity and density and less crack. Considering the applicability to real semiconductor manufacturing process, the reduction temperature should be decreased while increasing the reduction time. XRD patterns of tungsten films reduced at 400°C and 500°C for 60, 120 minutes are shown in Fig. 6. At 400°C, tungsten film was not reduced to metal tungsten film even after 120 minutes, while at 500°C, tungsten metal film was formed in 60 minutes.

From the results, by selecting proper organic solvent and



(a)



(b)

Fig. 5. SEM images of W metal films prepared at different reduction temperatures.
(a) 600°C, (b) 800°C.

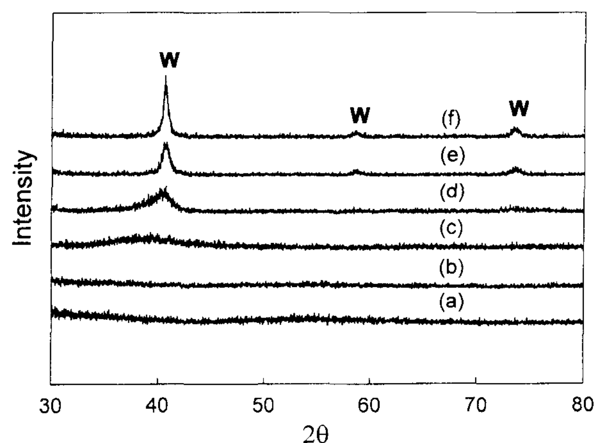
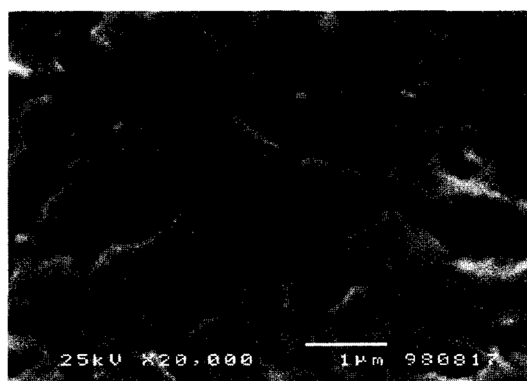
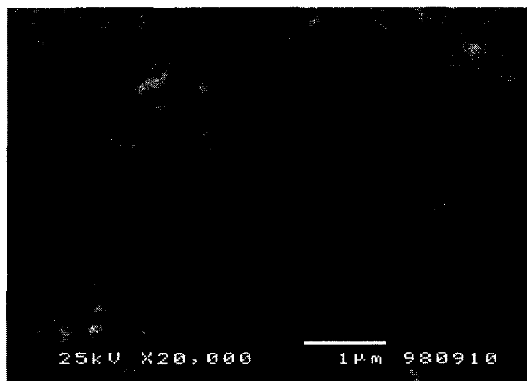


Fig. 6. XRD patterns of W metal films prepared at different reduction temperature and time.
(a) 400°C-30 min, (b) 400°C-60 min, (c) 400°C-120 min, (d) 500°C-30 min, (e) 500°C-60 min, (f) 500°C-120 min



(a)



(b)

Fig. 7. SEM images of W metal films prepared after reduction at 500°C for 120 min.
(a) without UV irradiation, (b) with UV irradiation (5.22 J/cm^2)

optimizing reduction conditions, tungsten metal films having good uniformity and density could be prepared by spin coating method. Thus the prepared tungsten metal film had much lower sheet resistance (2,300 μΩ·cm) than that of the film prepared without optimization procedure (36,000 μΩ·cm). But compared to those prepared by conventional CVD method (15 μΩ·cm), it still had high sheet resistance by 2 order of magnitude.

3.4. Properties of UV irradiated tungsten films

As mentioned above, tungsten metal film prepared by spin coating method had higher sheet resistance compared to those prepared by conventional CVD method, which might be explained due to the difference in uniformity and density. Okamoto *et al.* (1986) showed that W-IPA films could be used as an inorganic deep ultraviolet (UV), x-ray, and electron beam lithography resist. When soluble peroxotungstic film was irradiated by UV, polymerization took place to convert it to insoluble tungsten oxide film. Based on this mechanism, W-IPA films could be used as a negative lithography resist. In this work, with this aspect, by irradiating UV to W-IPA films before the reduction procedure, we tried to make films having higher uniformity and density due to the polymerization of the surface per-

Table 4. Characteristics of deposition processes

Characteristics	Evaporation	Sputtering	CVD	Spin Coating
Mechanism	Thermal Energy	Momentum Transfer	Chemical Reaction	Centrifugal Force
Deposition Rate (Å/min)	Very High (750,000)	Low (10)	Moderate (200~2,500)	Moderate (200~2,500)
Resistance (μΩ·cm)	15 (Mo metal film)		15 (W metal film)	300 (W-IPA film)
Energy Required	Low	High	High	Low
Metal Deposition	Yes	Yes	Yes	Yes
Cost	High	High	High	Low

oxopolytungstic compounds. Since the density of the tungsten atoms increases in the polymeric species, improvement of the film quality was anticipated. Electrical properties of the UV irradiated films were measured.

Before the reduction procedure, UV was irradiated to W-IPA films for 30 minutes and then the films were reduced at 500°C for 120 minutes. From the XRD patterns, metal tungsten films were confirmed to be formed. Furthermore, UV irradiated W-IPA films showed much lower sheet resistance (300 μΩ·cm) than that of films without UV irradiation (2,300 μΩ·cm) by 1 order of magnitude as expected. From SEM images presented in Fig. 7, UV irradiated metal films showed greater uniformity and density, which explained well the decrease of sheet resistance, even though it was still higher than that of prepared by conventional CVD method (15 μΩ·cm). In conclusion, as summarized in Table 4, spin coating method could provide potentialities to make electrically conductive metal films, not using expensive high vacuum equipments.

4. Conclusions

1. By applying the facts that tungsten metal is soluble in hydrogen peroxide, W-IPA solution could be prepared and spin coated on wafers. After proper reduction procedure, metal tungsten films were prepared without expensive high vacuum equipments.

2. N-methyl-2-pyrrolidone was found to be the most effective organic solvent to increase the uniformity and density of the W-IPA films formed.

3. By irradiating UV before the reduction procedure, films having greater uniformity, density, and lower sheet resistance could be prepared due to the polymerization of the surface peroxopolytungstic compounds.

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