High Purity Metal Production Using Dry Refining Processes

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Two different types of dry refining and bulk formation processes and thin film formation by the Gas Deposition Method have been studied using GD-MS, IGF-IR, N₂ Carrier Gas Extraction Method and CPAA, from view point of purification. Aluminum purification using liquid/solid phase under high vacuum and bulk formation of high purity tungsten by CVD method have been successfully achieved. The purity level of the purified aluminum is nearly 6N in metallics with extremely low hydrogen and oxygen contents (min. 40 ppb). The purity level of CVD-W succeeds more than 7N in metallics with extremely low oxygen contents (3.2 ppm) having high relative density 99.80%. Copper thin films formed by the Gas Deposition Method have higher purity, as purification mechanism works till and during film formation, and the resistivity of film, 20 nΩ·m, is very close to that of the bulk.

(Received August 6, 1999; In Final Form October 5, 1999)

Keywords: dry refining, high purity aluminum, chemical vapor deposition method, high purity tungsten, low gaseous contents, gas deposition method, gas evaporation method, copper thin film

1. Introduction

Many scientific and industrial efforts have been made on metal purification to enhance metal function and usage.¹⁻⁵⁾ One of major usages of highly purified metal is in thin film formation.⁶⁻¹⁰⁾ High purity metals and alloys have been applied in LSI (Large Scale Integrated Circuits) fabrication; quality of films prepared by sputtering and evaporation method reflects purity of source metals and alloys, for examples the high purity causes low resistivity.

Since the beginning of LSI industries, we have been supplying LSI manufacturers with pure aluminum pellets, pure sputtering targets including aluminum alloy, metallic silicide, pure titanium and pure tantalum and so on. Methods for purification, bulk metal formation and making targets are different and rather specific according to each metal, alloy or compound.

On the other hand, we have developed the Gas Deposition Method¹¹⁻¹³⁾ for making high purity films. Equipment named Jet Printing System (JPS) for the direct thin film formation has also been developed and is commercially available from VMC. This system consists of Ultra Fine Particles (UFP's) generation part, thin film deposition part, and attached units for controlling film formation speed and line film pattern. Using this system, designed width, thickness and pattern of film is obtainable.

In this report, some results on aluminum purification using liquid/solid phase^{4,5,14)} and on purification and bulk formation of tungsten using gaseous/solid phase¹⁵⁾ are described. Application of JPS for copper films and brief introduction to L-PVD (Laser-Physical Vapor Deposition; high melting point metal UFP formation by laser irradiation, tungsten as an example) are described.

2. High Purity Metal Production

2.1 Aluminum

In LSI devices, aluminum has widely been used as in-

terconnect material; such aluminum film is usually formed by sputtering. As the film quality reflects the purity of the sputtering target, demands for target having high purity (both metallic and gaseous) and well-controlled microstructure are very severe.¹⁴⁾ To supply LSI manufacturers with high quality aluminum targets, dry refining of raw materials, making ingot under clean vacuum melting, plastic deformation and heat treatment are standard, and the purity level is mainly determined by the results of dry refining process.

2.1.1 Experimental

High purity aluminum of two commercial levels (A and B, shown in Table 1), were used as raw materials and were purified by use of segregation method, which we called normal freezing; normal freezing means unidirectional solidification after full melting. Purification tests were conducted under the same solidification conditions but two different pumping conditions (under operation of diffusion pump and cryopump, respectively). The schematic of normal freezing is illustrated in Fig. 1. The furnace temperature was maintained constant at 750°C and removing speed was kept constant at 80 mm/h. After purification, the purified bars were cut at various positions (see Fig. 2), and the cut samples were rinsed with acetone, etched with HF + HNO₃ solution and rinsed with pure water and dried. Metallic impurities were analyzed by Glow Discharge Mass Spectrometry (GD-MS). Gaseous el-

Table 1 Impurity contents in raw material A and B.

	(ppm)					
	A	B	A	B		
Mg	0.702	0.028	U	5.3 ppb	<0.1 ppb	
Si	0.84	0.03	Th	18.3 ppb	<0.1 ppb	
P	2.24	0.01				
Fe	0.272	0.018	O	10	0.5	
Cu	0.34	<0.10	H	0.14	0.12	

Metallics: GD-MS

O: CPAA

H: N₂ Carrier Gas Extraction Method

Fig. 1 Schematic of normal freezing.

Fig. 2 Sampling position for analysis (a) Raw material, (b) Purified bar, (c) Purified bar.

elements (hydrogen and oxygen) were analyzed by N_2 Carrier Gas Extraction Method and Charged Particle Activation Analysis (CPAA¹⁶), respectively.

2.1.2 Results and discussion

The profiles of metallic impurity contents by points shown in Figs. 2(a) and (b), obtained from raw material bar and purified one by normal freezing under diffusion pump operation, are illustrated in Figs. 3 and 4. The purification effects in case of raw materials are clearly shown in Figs. 3(a) and (b) for A, and Figs. 4(a) and (b) for B, respectively. The raw material A has much impurity contents than the raw material B. It is however the same tendency to condense impurities much at the end (Tail in Fig. 1) and slightly at the top (Head in Fig. 1) of refined bar is confirmed in both cases. Condensation at the top is considered to happen trap phenomenon during first stage of solidification. Then the purification starts

Fig. 3 Impurity profiles in purified A.

Fig. 4 Impurity profiles in purified B.

Table 2 H and O contents in each bar.

		(in ppb)	
		H	O
1	Raw material A	140	10000
2	Raw material B	120	500
3	Purified A (with diffusion pump)	40	200
4	Purified B (with cryopump)	40	90
5	Purified B (with cryopump)	50	78
*6	Al-Cu Ingot C (with diffusion pump)	50	300
*7	Al-Cu Ingot D (with cryopump)	40	40

*6 Ingot C: using purified A (3)

*7 Ingot D: using purified B (4)

H: N₂ Carrier Gas Extraction Method

O: CPAA

and swept impurities are condensed at the end. The impurity levels at the end reaches more than 10 times higher levels compared to those in the raw material.

U and Th are requested to be excluded more severely, because these elements are the major emitter of α ray and thought to cause soft error. In both two raw materials A and B, U and Th contents are extremely low compared to other metallic impurities. Moreover, in case of raw material B, U and Th levels are equal or less than 0.04 ppb (see Table 1). Though the raw materials have extremely low impurity levels, the purification effects are also confirmed by the results of U and Th condensation at the end, and the top of the bar. By cutting off the end and the top of the bar, we can produce high purity ingot of aluminum and then supply high quality targets having very low metallic impurity, especially U and Th.

On the other hand, gaseous contents are reduced by a large pumping speed and very low base pressure. Analyzed data using samples shown in Figs. 2(a), (b) and (c) are summarized in Table 2, accompanied with data of Al-Cu ingot. Hydrogen contents in raw material are 120–140 ppb, irrespective of metallic impurity level. Hydrogen is known to be hardly evacuated with diffusion pump and cryopump. According to Ohnishi,¹⁷⁾ hydrogen contents are 0.09–0.27 ppm, irrespective of pure aluminum and aluminum alloy. But the results indicate that hydrogen contents are reduced by vacuum melting and reach quasi plateau level 40–50 ppb. This level is about 1/3 of the raw material level. Oxygen contents are considered to change from 500–10000 ppb (This difference reflects the grade of raw materials). The pressure ranges are 0.67–0.24 mPa (5.0–1.8 μ Torr) in case of No. 3, 0.53–0.10 mPa (4.0–0.72 μ Torr) in case of No. 4 and 0.06 mPa (0.46 μ Torr) in case of No. 5. These high oxygen contents are easily reduced by melting under high vacuum, where cryopumping is recommendable. The resulting oxygen contents were 200, 90, and 78 ppb, respectively.

2.2 Tungsten

High purity tungsten is also required in LSI fabrication. As tungsten has high melting point, bulk tungsten is usually made by powder metallurgy (P/M) process, which results in limitation of purity ($\sim 5N$) and density ($\sim 90\%$). The process improvement raises the density limitation up to 99%,^{18,19)} but the purity itself is being kept $\sim 5N$. To achieve higher purity and higher density of tungsten, Chemical Vapor Deposition (CVD) process is usable.

2.2.1 Production principle and sample preparation

Solid tungsten is made by reduction of gaseous WF₆ with gaseous hydrogen at several hundreds °C. The following is its chemical reaction formula.

This reaction means “direct solid formation from gas.” Therefore, gas purity and other contamination source control are the keys in order to obtain high purity bulk plates. The density of tungsten made by CVD process is determined by gas feed rate and substrate temperature. CVD-W reaction chamber to make bulk tungsten plates is illustrated in Fig. 5. After finishing operation, samples were cut from the plates and analyzed. Impurity analyses were made by GD-MS, IGF-IR, IR and CPAA. Density measurement, microstructure observation, and XRD analysis were also performed.

2.2.2 Results and discussion

Metallic and gaseous impurities are analyzed in 20 samples cut out of CVD-W plates and results are summarized in Table 3. The metallic impurity levels are low enough (ppb level or below) to guarantee 7N. The impurity level of the CVD-W is two orders of magnitude purer compared to those of high purity tungsten fabricated by P/M method: the commercial base high purity tungsten powder has the purity level $\sim 5N$ in metallics. The gaseous impurity levels were also extremely low: 10–20 ppm $\sim$ the detectable limit of IGF-IR. Oxygen content was only 3.2 ppm by CPAA analysis (more accurate analysis for lower Oxygen contents). These results on impurity analysis from over 20 samples suggest that our CVD process has good reproducibility.

Density measurement was also performed on 20 samples and the results were summarized in Fig. 6. These results also suggest good reproducibility. The average relative density of

Fig. 5 Schematic of reaction chamber.

Table 3 Impurity contents in high purity tungsten.

Unit	ppb													ppm		
20 samples	Li	Na	K	Mg	Ca	Al	Si	Cr	Fe	Ni	Cu	Mo	U	Th	O	C
Internal spec.	≤10	≤10	≤10	≤10	≤10	≤10	≤10	≤10	≤10	≤10	≤10	≤10	≤0.2	≤0.2	≤30	≤30
Analytical Method	GD-MS													IGF-IR		IR
Max.	<1	2	3	<1	<1	3	2	<1	<1	<1	<1	<1	<0.1	<0.1	20	10
Min.	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<0.1	<0.1	10	<10

Fig. 6 Relative densities of high purity tungsten.

Fig. 7 Sampling position for microstructure and XRD.

Fig. 8 Microstructure of CVD-W.

Fig. 9 XRD patterns of CVD-W.

20 samples was 99.8%. The level of these relative densities is comparable to the levels obtainable by melting and higher than that of commercial base high density tungsten (99%).

Microstructure and texture of CVD-W were also observed and analyzed, using samples shown in Fig. 7. Surface and cross-sectional view in Fig. 8 shows that CVD-W has columnar structure like dendritic growth, as expected from heat transfer direction. This microstructure is completely different from that of tungsten made by P/M process. XRD patterns shown in Fig. 9 indicate that preferred orientation of crystalline growth $\langle 100 \rangle$ takes place in CVD process and show good agreement with the results shown in Fig. 8.

3. Direct Metal Thin Film Formation

A new film forming process called the Gas Deposition Method¹¹⁻¹³⁾ has been developed at VMC. The method has the following advantages.

- (1) Dry and low contamination process
- (2) Low temperature process (lower than 300°C)
- (3) Maskless high speed direct patterning process

The schematic drawing of this method is shown in Fig. 10. UFP's are formed by the gas evaporation method²⁰⁻²²⁾ in an evaporation chamber which is filled with He gas about 0.067–0.1 MPa (500–760 Torr) and carried through a transfer pipe to

a deposition chamber evacuated constantly by vacuum pump below 1330 Pa (10 Torr). The velocity of UFP's at the nozzle which is located at the end of transfer pipe is several hundred meters per second. And, UFP's collide with a substrate in the deposition chamber because the pressure difference between two chambers accelerates the mixture of gas and UFP's. A film is formed continuously by the collision of UFP's to the substrate and patterned by means of moving the stage that holds the substrate.

Two types of the evaporation heating source shown in Fig. 10; (a) a laser heating source for high melting point metals,^{23,24)} and (b) an induction heating source for comparatively lower melting point metals. Tungsten raw material of VMC has been used for the laser heating deposition. The high purity materials of VMC has been used for aluminum and copper film deposition by induction heating in order to produce high quality film with resistivity close to those of bulk materials.

3.1 Introduction of UFP's formation by laser irradiation

UFP's formation of high melting point metals, tungsten, tantalum and molybdenum, by laser irradiation has been studied with the support of the R&D Institute of Photonics Engineering entrusted from the Advanced Photon Processing and Measurement Technology Program of the New Energy and Industrial Technology Development Organization of Japan.

Tungsten UFP's were produced by the irradiation of two synchronized pulse Nd:YAG lasers on tungsten substrate under low pressure He gas atmosphere as shown in Fig. 10(a). One of the lasers, called assistant laser (max. power: 150 J/P, wavelength: 1064 nm and 10 ms pulse width), is used for heating up a sample. Another laser, called main laser (max. power: 10 J/P, wavelength: 1064 nm and 0.2 ms pulse width) is for evaporation of the sample. Main laser is irradiated delaying 9 ms, after start of the assistant laser irradiation. Experimental conditions were as follows. The high purity tungsten plate was prepared as a specimen for laser irradiation in order to avoid fracture by thermal shock. The main laser power was 10 J/P and the assistant laser power was 46.5–132 J/P to produce UFP's efficiently under the 13–670 HPa of He gas. The primary particle size of several nm of tungsten UFP's were formed and their size distribution was measured by a low pressure differential mobility analyzer. The result shows that the size distribution and shape of UFP can be controlled by pressure and laser power condition. The detailed discussion is found in another articles.^{23,24)}

3.2 Copper film formation by the gas deposition method

Impurity levels of copper films, produced by the Gas Deposition Method of induction heating source, were measured by use of GD-MS. Two types of copper pellets, 4N (raw material before purification) and 5N (purified products) were tested as raw materials for the films. Copper pellets were charged in a pyrolytic carbon crucible, and He gas of 6N-purity was prepared by the He purification recycling system. The crucible was heated at 1780°C in 800 HPa (600 Torr) of He atmosphere for evaporation and the copper films were formed in the deposition chamber at 160 Pa (1.2 Torr).

An example of copper film having coil pattern shape;

(a) Laser Irradiation

(b) Induction Heating

Fig. 10 Schematics of UFP generation apparatus (a) Laser Irradiation, (b) Induction Heating.

Cu Line Pattern

Fig. 11 Pattern samples of Cu film.

Table 4 Impurity contents in raw material and GD films.

Element	4N Cu		5N Cu	
	Raw material	GD film	Raw material	GD film
P	1.35	0.01	0.88	0.01
S	5.5	0.54	1.11	0.45
Mn	0.16	0.09	0.09	0.07
Fe	0.66	0.2	0.72	0.52
Ni	0.4	0.16	0.42	0.12
As	0.16	0.02	0.18	0.01
Ag	5.34	4.02	1.86	0.34
Sb	0.13	0.01	0.08	0.01
Cr	0.07	0.12	0.06	0.06

(GD-MS)

30 μm of thickness, 130 μm of line width and 90 μm of line space, is shown in Fig. 11. In order to analyze impurity in the films, 25 mm square copper films of 0.3 mm thick were formed on silicon wafer. The resistivity of copper films was measured by 4 point probe method and its value was 20 $\text{n}\Omega\cdot\text{m}$. The impurity level, copper raw materials and its films, is summarized in Table 4. It is easily recognized that the impurity levels in films are reduced compared to those in raw materials.

Impure materials having high vapor pressure are evaporated first before the temperature of the crucible reaches set-point to deposit the copper film. In order to avoid the contamination in the atmosphere of the system and on the substrate, the entrance of transfer pipe is located away from the crucible and the vapor of contaminated element is evacuated through an evacuation pipe, on the other hand, only clean He gas passes through the transfer pipe. On depositing the copper, the transfer pipe is set right above the crucible and this mechanism also works as a shutter system to pattern the film. In Table 4, elements of lower vapor pressure are reduced since their amount is much less than that of copper during the deposition and left in the crucible. This means that the Gas Deposition Method is advantageous for making high purity thin film.

4. Summary

Both metallic and gaseous impurities in aluminum are effectively purified by dry refining processes and the metallic purity of aluminum reaches almost 6N and the hydrogen and oxygen contents are reduced to about 40 ppb.

High purity tungsten plates are successfully formed. The purity level succeeds more than 7N in metallics and less than 10–20 ppm in gaseous elements.

Tungsten UFP's are successfully formed by L-PVD. High purity tungsten plates must be used to produce UFP's without fracture by thermal shock.

Copper thin films made by Gas Deposition Method have higher purity than those of raw materials and typically have resistivity 20 $\text{n}\Omega\cdot\text{m}$, very close to that of bulk one.

Acknowledgement

Authors acknowledge K. Nakajima of UMAT to his active support for impurity analysis, and also acknowledge to O. Itasaka and S. Oka of VMC to their support for modifying Figs., Tables and sentences.

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