INDUSTRIAL PRODUCTION OF HIGH PURITY TITANIUM BY THE IMPROVED IODIDE PROCESS

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Abstract

We have produced titanium of 99.999% purity on the 50-100kg per batch scale by the improved iodide process. Unlike the conventional wire filament process on a kilogram scale, we use high purity titanium tube as a deposition substrate. Iodide titanium deposits on an outer surface of the tube,while its inner surface is indirectly heated by a graphite heater. In this way deposition surface area is greatly enlarged by an order of two as compared with the conventional iodide process. A diffusion pump evacuates the inner part of the deposition tube at a pressure bellow 10^{-1} Pa to prevent contamination of titanium from the graphite heater.

1. Introduction

With the rapid increase in the degree of Large-Scale Integration (LSI) in recent years, dimensions of solid state electronic devices are getting smaller and smaller. As a result materials used in such devices require higher purity and strength. Due to the present demand for a remedy to the signal delay caused by the increase in electrode wiring resistivity and electromigration in fine metal interconnects, the focus is now being placed on refractory materials with lower resistance and higher purity, compared to the frequently used polysilicides. Metallic materials with the above properties which can be utilized as electrodes in LSI are molybdenum, tungsten, and titanium or their silicides. Among them titanium is particularly desirable due to its excellent specific strength, workability and corrosion resistance.

However, as an electrode material for semiconductors, titanium metal must be of very high purity. Impurities in titanium which affect the performance of LSI devices are alkaline metals (Na, K), radioactive metals(U,Th), and heavy metals (Fe, Ni, Cr). Impurity contents that are allowable for semiconductor materials are respectively Na, K < 20 ppbw, U, Th < 1 ppbw, and Fe, Ni, Cr < 1 ppmw. One of the typical methods of obtaining high purity titanium is the thermal decomposition of titanium iodides, which was first studied by Van Arkel and de Boer in 1925-1930[1]. In the iodide process, the decomposition scheme is described as follows,

$$\text{crude Ti} + 2I_2 \text{ ---> } TiI_4 \text{ (synthetic reaction)} \quad (1)$$

$$TiI_4 \text{ ---> high purity Ti} + 2I_2 \text{ (thermal decomposition)} \quad (2)$$

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A crude titanium reacts with iodine to form a titanium tetraiodide at temperatures of 500-800 K. The thermal decomposition of the titanium tetraiodide proceeds on a deposition substrate which is usually a wire-filament resistively heated at temperatures of 1400 to 1800 K. The iodine liberated returns for further reaction with the crude titanium. A series of reactions involving iodine go on in a cyclic way . Using the above process, high purity titanium can be easily obtained, however, its productivity is very low because of the use of a fine filament as the deposition substrate. Our aim is to develop a new technology for obtaining high purity titanium at high production rates with a lower decomposition temperature.

2. New technology for producing high purity titanium

2-1. Reaction conditions

In the conventional iodide process, titanium tetraiodide is directly decomposed to titanium , which causes high temperature decomposition at 1400-1800 K. On the other hand, titanium refining in our iodide process involves reactions of crude titanium with titanium tetraiodide, thereby synthesizing lower valent titanium iodides , and decomposing the lower valent titanium iodides to high purity titanium. The lower valent titanium iodides , i.e., TiI_2 and TiI_3, afford higher synthetic reaction temperatures and lower thermal decomposition temperatures, as compared with titanium tetraiodide. While the reaction mechanisms for the synthesis and decomposition of the lower valent iodides are indistinct, the reactions may be represented by the following equations:

$$\text{crude Ti} + TiI_4\text{(or I)} \longrightarrow TiI_2, TiI_3 \text{ (synthetic reaction)} \qquad (3)$$

$$TiI_2, TiI_3 \longrightarrow \text{high purity Ti} + \text{I (thermal decomposition)} \qquad (4)$$

The lower valent titanium iodides are synthesized at about 1000-1200 K. These iodides undergo thermal decomposition more readily than titanium tetraiodide, allowing the thermal decomposition temperature to be lowered to 1400-1500 K. Accordingly, the possibility of thermal decomposition of metal impurities contained in the iodides is more greatly reduced than that at higher decomposition temperatures.

2-2. Improvement of titanium productivity

The rate of titanium deposition is known to be limited by the diffusion of iodine and iodides, i.e.,natural convection in the reaction space[2]. Therefore, to attain high titanium productivity, the enlargement of deposition surface area is needed. We used a titanium tube as a deposition substrate instead of a conventional wire filament. Titanium deposits on the outer surface of the tube , while the inner surface was indirectly heated by a graphite heater. The power supply to the tube was not affected by the deposition rate of titanium, and the uniform temperature distribution in the axial direction was attained. By evacuating the heater chamber with an oil diffusion pump, the deposited titanium was free from contamination from the graphite heater. Since the tube permits its diameter and length to be arbitrarily selected, the deposition surface area can be drastically increased in comparison with that of the filament. In addition, the change in the surface area is relatively small as the reaction proceeds, thereby it is easy to maintain the deposition conditions constant.

3.Experimental

3-1. Small scale production of titanium

Preliminary investigation of purification in the iodide process was carried out using a small scale reactor. Figure 1 shows the schematic outline of the apparatus. The reactor made of Inconel tube (250 mm I.D.x1000 mm length) was lined with Ta sheet on its inner surface to prevent corrosive reaction of iodine with Inconel. A titanium tube (43 mm O.D.x 700 mm length) was used as the deposition substrate. The tube was made of 99.998% pure titanium, and its thickness was 1 mm. The tube was heated to 1400 K by a graphite heater installed inside it. The tube was evacuated through a combination of oil diffusion and rotary mechanical pumps to prevent contamination from the graphite heater. About 50 kg of crude titanium was stacked cylindrically in the annular space between the reactor wall and the titanium tube.

Commercial titanium tetraiodide(99.7%) was used as a feeding material without further purification. Titanium tetraiodide was introduced into the reactor which was evacuated and heated to 1-10 Pa and 1150 K,respectively. In this way the titanium tetraiodide reacts with the crude titanium to form lower valent titanium iodides(TiI_2, TiI_3). The iodides were transported to the surface of decomposing tube by gas diffusion, and high purity titanium deposited on the outer surface of the tube. By-products(iodine and TiI_4) again react with the crude titanium to form subiodides. The titanium tetraiodide and subiodide gases repeated these reactions as they traveled up within the reactor and were finally condensed and captured by a trap which was cooled with liquid nitrogen.

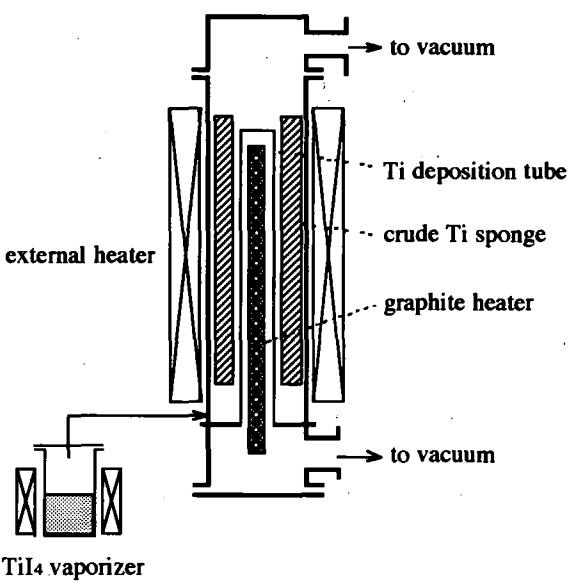

Figure 1 - Schematic outline of the small scale reactor

Starting with the crude titanium sponge of 99.98% purity, the reaction was kept 200 h. We obtained 6.5kg polycrystalline titanium deposit, part of which is shown in Figure 2. Its thickness was about 12 mm and the deposition rate was 1 μm/min. We melt the titanium deposit together with the original substrate by an Ar plasma arc. The analyses of various impurities in the crude

titanium sponge and the titanium deposit are given in table I. Refining effect was prominent especially for Fe, Ni, Al, and O. Carbon contamination from the graphite heater was negligibly small.

Figure 2 - Titanium deposit produced by the small scale reactor

Table I Typical analysis of crude titanium sponge and deposited titanium

Element	crude Ti sponge(ppm)	deposited Ti(ppm)
Fe	50	0.5
Ni	15	0.1
Cr	8	0.4
Al	7	1.1
Si	3	0.4
Na	<0.02	<0.02
K	<0.02	<0.02
U	<0.001	<0.001
Th	<0.001	<0.001
C	30	30
H	<10	<10
O	300	80
N	10	10

3-2. Large-scale production of titanium

Based on the results of the small scale reactor, we made a design for large scale apparatus with titanium productivity of 50-100 kg/Bt. The flowsheet was similar to that employed for the small

scale. The reactor was made of SUS, whose diameter and height were 500 mm and 2700 mm ,respectively. The titanium deposition tube (210 mm O.D.x 2000 mm length) was hung and fixed with its upper flange being sealed. The tube was heated by a graphite heater using a three-phase transformer. The diameter ratio of the reactor and the deposition tube was small, as compared with that of the small scale one. As a result, the temperature of the crude titanium was strongly affected by the heat dissipated from the graphite heater and the temperature gradient from the deposition surface toward the titanium sponge became gradual. As the formation and decomposition of the iodides occur at different temperatures in the same reactor, it is necessary to make steeper temperature gradient toward the radial direction of the deposition tube. We lowered the temperature of outer surface of the reactor by air-cooling.

The titanium sponge was transformed to cylindrical-shape compact by compression and then stacked surrounding the deposition tube annularly. The temperature of the deposition tube, measured by a thermocouple attached to its outer surface, was kept at 1400 K. The surface temperature of the reactor gradually rose up to 1300 K without cooling. Forced air blowing was done to maintain the surface temperature below 1200 K.

We have started carrying out short-period titanium deposition experiments. Figure 3 shows a fraction of the deposited polycrystalline titanium. The experiment was conducted for 190 h, and we obtained 65 kg titanium deposit. The deposition thickness attained to 10-12mm, corresponding to the deposition rate of 0.9-1.1 μm/min. The deposition rate of the large scale reactor was comparable to that of the small scale one. Preliminary chemical analysis indicated the following levels of impurities: Fe=1 ; Ni<1 ; Cr<1 ; Al<2 ; C=30 ; O=80 ; N=10 ppmw. Gaseous impurity contamination such as oxygen and nitrogen may be caused from leaks in the reactor or desorption of gases from the titanium compact. The longer the deposition period, e.g., 300-400 h, the lower the metallic impurity contents. The proportional ratio of the impurity content of original tube to deposited titanium is expected to come close to negligible, however a complete evaluation has not been made at current stage.

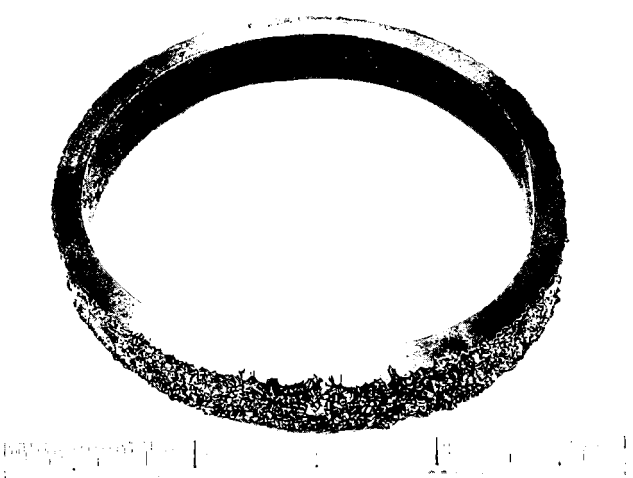

Figure 3 - Titanium deposit produced by the large scale reactor

4. Conclusion

An attempt was made to improve the productivity of high purity titanium by a newly developed iodide process . Unlike the conventional iodide process, we used a high purity titanium tube as a deposition substrate. The deposition surface area was able to be enlarged by an order of two, compared with the conventional wire filament process.

a) small scale reactor
Operation of 200 h produced a 12 mm thickness titanium deposit with a rate of 1 μm/min. It weighed 6.5 kg. The deposit was observed to contain Fe=0.5 ppmw, Al=1.1 ppmw, O=80 ppmw, Na<0.02 ppmw, etc.

b) large scale reactor
Operation of 190 h produced 65 kg titanium deposit with a thickness of 10-12mm. The deposition rate attains to 0.9-1.1 μm/min. At the present stage we tried a short period operation, however, we can expect more than 100 kg titanium deposit in a period of 300 h.

5. References

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(2)G. H. Kesler, Trans. A.I.M.E.,218(1960),197