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TUNGSTEN TITANIUM TARGETS FOR VLSI DEVICE FABRICATION

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We believe the future of technology is highly dependent on the continuous development of advanced materials and deposition techniques. Over the years, we have dedicated ourselves to advancing these technologies and have developed strong linkage with our clients by providing them with the best in both thin film materials and deposition systems.

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ABSTRACT

Through-life tungsten titanium, W-Ti, target performance is reported showing that target configuration affects resistivity and composition roll-off while method of manufacture and microstructure (amount of "β(Ti,W)") have little affect on particulate generation. High density is the most critical parameter affecting particulate generation and different consolidation techniques which are capable of producing high density materials yield differing microstructures.

INTRODUCTION

Since it was commercialized by Materials Research Corporation (MRC) in **1970,** tungsten – titanium, W-Ti (or commonly referred to as TiW), has been used extensively in semiconductor fabrication as a diffusion barrier layer and as a capping layer in interconnect metallization. Pure W-Ti behaves as a passive barrier when interposed between aluminum or tungsten and silicon. Barrier performance is further enhanced when the layer is "stuffed" by sputtering reactively in the presence of nitrogen or by exposing the deposited film to air. The drive toward minimal C-V shift has lead to improvements in the control of contamination, particularly mobile ions such as sodium and potassium which today are found at levels lower than **70** ppb. Oxygen contamination is generally found to be less than **1000** ppm.

Continuing device miniaturization has imposed new challenges on the target manufacturers to provide ever higher quality W-Ti targets which consistently produce defect-free films throughout target life.

Particulate generation during the use of W-Ti sputtering targets is the subject of a number of recent studies by target manufacturers. These targets are made by a variety of powder consolidation methods including: inert gas hot pressing (IGHP), hot isostatic pressing (HIP) and cold isostatic pressing/sintering (CIP/Sinter). Advocates of the various techniques have each emphasized the value of their particular equipment or methods in minimizing particulates.

Waterman et al.' and Dunlop et al.[2] compared hot pressing, vacuum hot pressing and hot isostatic pressing concluding that vacuum hot pressing is the preferred technique. Wickersham et al.[3] suggested that hot isostatic pressing is superior to a cold press and sinter technique. These groups propose mechanisms to explain the improved sputtering performance claim. In each case, however, the density of the target is not given sufficient attention as a critical parameter for particulate generation.

These recent studies are based upon broad assumptions and on data that is not related to the actual semiconductor experience. This paper will review actual in-the-fab through-life target performance. It will review previous work which relates target characteristics to particle generation, and the effects of microstructure and density on particulate generation from W-Ti sputtering targets.

EXPERIMENTAL PROCEDURES

At a 0.8 μm CMOS semiconductor production facility, through-life (up to more than 700 kW-hr) performance of three conical high performance Eclipse'" W-Ti sputtering targets were compared. The targets were made by three different manufacturing processes: IGHP, VHP and hot pressing (HP). The metallurgical characteristics including metallic purity, oxygen content, density and microstructure were evaluated, Table 1. The targets were sputtered under the conditions listed in Table 2.

TABLE 1: SPUTTERING TARGETS

Process	Metallic Purity (%)	Oxygen Content (ppm)	Density (g/cm^3)	β-TiW
IGHP	99.9980	680	14.58	Y
VHP	99.9979	250	14.51	Y
HP	99.9949	1700	13.68	N

TABLE 2: SPUTTERING CONDITIONS

Power:	3.0 kW
Base Vacuum:	5 x 10-7 Torr
Ar Purity	99.9995 %
Ar Pressure:	10 mTorr
Ar Flow Rate:	100 sccm
Wafer Temp:	300°C
Nominal Thickness:	3000 A
Deposition Rate:	50 to 30 A/s

For metallographic examination, samples were polished and etched using a two step process. The W was revealed using a Murakami etch and the Ti was etched using and aqueous 2% HF t 4% H_2O_2 solution. An ISI scanning electron microscope (SEM) was used to examine the microstructure of TiW sputtering targets. The technique provides atomic number contrast to distinguish between phases that are rich in either tungsten or titanium.

X-ray diffraction, employing a computer controlled Rigako DMAX system, was used to detect phase differences. Samples were scanned from 30° to 110° of 2Θ in 0.2° steps with a 0.4 second count time.

Thin film properties were monitored utilizing standard fab practices. Film thickness was measured using profilometry and film sheet resistivity was measured using a a-point probe. X-ray fluorescence was used to determine film composition. Reflectivity was measured using a GAM densitometer. Particle measurements were conducted with a Tencor Surfscan 4000 instrument. The measurement technique involves laser beam scattering from the coated surface to detect and count particles.

RESULTS & DISCUSSION

FILM PROPERTIES

A linear relation between film resistivity and film Ti content exists, Figure 1. The combined through-life data are compared to previously collected data for a variety of target compositions (3 to 13 wt% Ti), configurations (planar magnetron, conical, full erosion rotating magnet) and sputtering systems (batch and single wafer cassette to cassette). It is seen that the linear relation is a material property and is independent of manufacturing method, target style or sputtering method. Vacuum quality and process conditions which may alter film purity or structure can affect the resistivity.

Figure 2 shows that the Ti content in the films decreases through life from 7 to 3.5 wt% and causes a decrease in the bulk film resistivity of the film from 50 to 37 $\mu\Omega$-cm. These effects stem from increased scattering in the plasma as the target erosion depth increases and the plasma becomes more focused. When employing a full erosion zone style target such as an MRC RMX'", the fall-off in film resistivity is minimized, Figure 3. In this configuration a deep focusing erosion zone is eliminated.

The reflectivity of all films was constant throughout target life, Figure 4.

W-Ti TARGET MICROSTRUCTURE AND PARTICLE GENERATION

Previous reports[2,3] attempted to correlate the existence of a "β(Ti,W)" with particulate generation. The authors of Reference 2 performed microstructural analysis with X-ray diffraction and energy dispersive X-ray analysis (EDAX). These techniques can confirm the phases and structure present. However, the findings were poorly interpreted. The authors of Reference 3 assessed the amount of "β(Ti,W)" with an optical microscope. This technique is only acceptable as a supporting technique when used with others to distinguish between phases. Thus, because a clear interpretation of the microstructure of W-Ti sputtering targets has not been developed, a definition is necessary of what is meant by "β(Ti,W)" and what, if any, role it plays in the generation of particulate from sputtering targets.

DEFINING **"β(Ti,W)"**

"β(Ti,W)" is an area in the microstructure consisting of finely dispersed tungsten within titanium. Thus, instead of one "phase" it actually contains two phases. This microstructure is the result of a solid-state precipitation, eutectoid reaction. This can be explained with the use of the Ti-W phase diagram[4], Figure 5.

Solid tungsten exhibits a body centered cubic (bcc) structure from room temperature to its melting point. Pure titanium has an hexagonal closed packed (hcp) structure at room temperature and transforms to bcc at 885°C. The phase diagram shows, that for temperatures above 740°C, a 10, wt% titanium alloy will consist of a single P-phase solid solution. The inherent assumption in the use of phase diagrams is that a state of equilibrium is attained. Achieving equilibrium for a W-Ti system would require sufficient time at elevated temperature for diffusion to homogenize the distinct regions of Ti and W that exist in the original powder. To varying degrees, this diffusion occurs during consolidation to establish local regions of near equilibrium compositions.

In commercially available sputtering targets, equilibrium is not attained since tungsten and titanium are not uniform throughout the structure. Diffusion of tungsten into regions of titanium tends to produce areas represented by the titanium-rich region of the phase diagram. As these titanium-rich areas cool, the solubility of tungsten in titanium drops, precipitating tungsten. This fine lamellar distribution of tungsten in the surrounding titanium is called "β(Ti,W)".

Figures 6a and 6b show the microstructure for an inert gas hot pressed target and a vacuum hot pressed target, respectively. These secondary electron images show contrast by atomic number differences between titanium (atomic number 22) and tungsten (atomic number 74). The low magnification micrographs shows the two distinct phases of titanium (dark areas) and tungsten (light areas).

Although the vacuum hot pressed sample was fabricated utilizing the same process as described by in References I and 2, the resultant microstructure is quite different from that reported. While the microstructure appears similar to that reported at low magnification, at high magnification, this material exhibits precipitated W along the Ti grain boundaries and diffusing into the bulk of the Ti grains. The Ti-rich regions are not single phase as reported, but show lamellar β(Ti,W) formed around the circumference of, along the grain boundaries between and within the bulk of Ti-rich regions.

A similar lamellar microstructure is not observed in the inert gas hot pressed sample. Elucidation of this microstructure is provided below.

Further independent confirmation of the phases present in W-Ti targets is shown in Figure 7. X-ray diffraction patterns from samples of various commercial W-Ti targets were collected. The results show the existence of only one bcc phase, while the phase diagram predicts two and metallography shows two distinct phases. This apparent contradiction can be explained by the similarity of the lattice parameter, a,, which is the specific distance between neighboring atoms in the structure, for both bcc titanium and tungsten:

	TEMPERATURE 25°C	TEMPERATURE 900°C
Ti	Structure = HCP a = 2.950 A c = 4.686	Structure = BCC a = 3.32 A
W	Structure = BCC a = 3.165 A	

The fact that o-titanium (hcp) is not detected by X-ray diffraction at room temperature suggests that tungsten acts like other known p-phase stabilizers. Elements including, molybdenum, tantalum, vanadium and niobium act to preserve the bcc phase of Ti at room temperature. From the results in Figures 6 and 7, the type of microstructure that previous authors claim is "β(Ti,W)" is likely to consist of stablized p-titanium with tungsten precipitates.

The microstructure, Figure 6a, of the inert gas hot pressed material, shows no reaction products in the Ti-rich areas. The quantity of tungsten dissolved and diffused into titanium during consolidation was not sufficient to exceed the solubility of tungsten in titanium. However, from the X-ray data in Figure 7, the quantity of dissolved tungsten is sufficient to stabilize the bcc form of titanium at room temperature and appears to be isomorphic with tungsten.

PARTICLE PERFORMANCE

Particle performance was measured in an Eclipse'" sputtering system for each target making process by counting particles greater than 0.5 μm. Device yields were also measured. No statistically significant difference in particle yields were measured for devices from wafers produced with the two higher density targets, Figure 8. The particle performance is independent of the manufacturing process (method of consolidation of metal powders) and oxygen content of the targets for oxygen levels below 1000 ppm for targets with the highest density. The third target, HP, produced a significantly higher particle count. Although the oxygen content is somewhat higher than the other two targets, it is believed that the observed differences in particulate levels is in direct relation to the density of the targets.

A direct correlation of particle count with target density is exhibited. The trend line of average particle density versus target density for the through-life data, Figure 9 agrees with previous data[5] indicating that the use of higher density targets can result in lower particulate levels.

Early target life (<200 kW-hr) data of Reference 3 are also plotted in Figure 9 and are seen to follow the same trend. The lowest level of particles from W-Ti targets stem from the highest density sputtering targets. The authors used hot isostatic pressing to consolidate the part, using both temperature and pressure as variables. These variables influence the density of the target. From their reported data, Figure **10,** the authors attributed low particulate generation to targets produced by low temperature hot isostatic pressing, a method which avoids the formation of "β(Ti,W)". On the other hand, both IGHP and VHP targets are consolidated at high temperature in the regime where one can generate "β(Ti,W)". This regime is illustrated by the shaded region in the figure and it suggests that consolidation temperature alone is not the critical variable. Although the target density is shown to be the critical parameter such a comparison was not developed or examined in Reference 3.

It is important to note that the through-life data show the positive impact of high density on particle generation. This contrasts the contention by the authors of reference 3 that particle generation from sputtering targets is significant only during the initial stage of target life and that particle levels during the remainder of target life are dominated by "flaking" in the sputtering system

The differences in the slopes of the two sets of data in Figure 7 may be due to the combined effects of the target and the system maintenance. For modern sputtering equipment, the "incubation period" for flaking is the time during which particle generation is predominantly related to the target. During this period the generation of particles is lowest. The techniques for extending the incubation for flaking are: specially designed and treated shielding; slow roughing and venting flows to and from vacuum; filtered gases; and special handling of wafers from the cassette to a loadlock. Flaking can also be reduced with proper maintenance. The combined particulate performance over the life of the target is influenced by the design of the system, the quality and frequency of maintenance, and the target density.

The through-life particle performance data for this study, Figure 11, and in a separate study, Figure 12, show little difference between inert gas hot pressed targets and vacuum hot pressed targets. These results are in direct conflict with the results reported in reference 2 where it is suggested that vacuum hot pressed targets generate fewer particles than either inert gas hot pressed or hot isostatically pressed material. The authors believe that the data for vacuum hot pressed represents the particle contribution of the target, while the data for the other consolidation techniques reflect contributions of flaking from shields and the chamber. If so, these data are not a true comparison of the different target manufacturing processes. The excursions in particle counts shown in Figures **11** and 12 occur at intervals of routine maintenance.

It is apparent from the available data that although different consolidation techniques can produce different microstructures, a number of these techniques are capable of producing high density targets which produce low levels of particles.

QUALITY IS THE KEY

In this study, no significant differences in device yields were measured. However, with further reductions in line widths, particulate levels will certainly reduce device yields.

A high process capability illustrated in Figure 13 demonstrates the manufacturing consistency required produce high density W-Ti targets for current and future semiconductor interconnection applications, strong adherence to statistical process control methods, clean powder metallurgical manufacturing and computer automation are keys.

CONCLUSIONS

1. A linear relation between film resistivity and film Ti content exists, is a material property and is independent of manufacturing method, target style or sputtering method.

2. Film Ti decreases through life with a corresponding resistivity roll-off due to focusing of the plasma as a deep erosion zone is formed.

3. Use of a full erosion zone style target such as an RMX'" minimizes Ti and resistivity roll-off.

4. The density of W-Ti sputtering targets is confirmed by multiple investigators to be a critical parameter affecting the contribution of the target to particles generated during sputtering.

5. Different consolidation techniques can produce different microstructures in W-Ti sputtering targets, yet a number of these techniques are capable of producing a high density sputtering target.

6. Care and attention to maintenance and general housekeeping contribute substantially to reducing particulate levels.

BENEFITS

High density TiW sputtering targets provide assurance to semiconductor manufacturers that the particle levels generated directly from the sputtering target are the lowest possible. Reduced levels of particulates attributable to any source improve yields at the metallization step of wafer fabrication process. In addition to improved particle performance, higher sputtering target densities promote faster pump down of the target to vacuum, and reduce the likelihood of contamination from ambient air.

REFERENCES

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Figure 1. The linear relation between film resistivity and film Ti content is a material property which is independent of target composition (3 to 13 wt% Ti), manufacturing method (IGHP, VHP, HIP), target style (planar magnetron, conical, full erosion rotating magnet) and sputtering systems (batch and single wafer cassette to cassette).

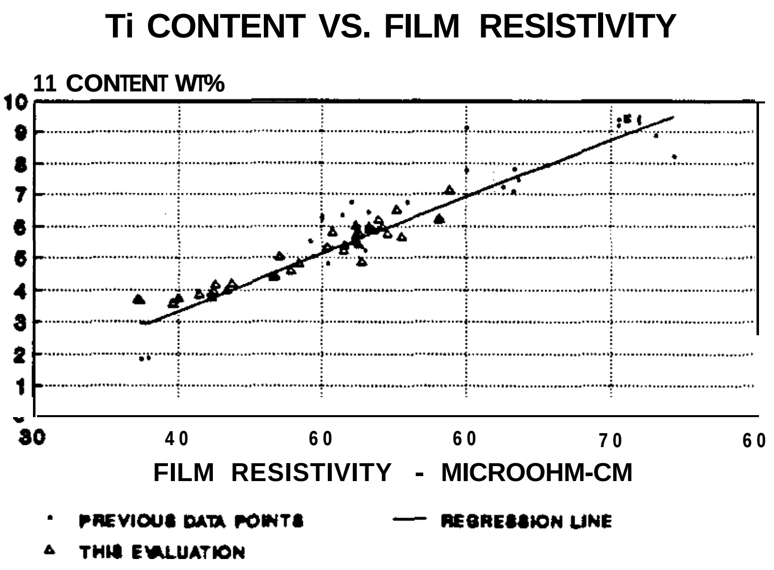

Figure 2. With W-Ti conical style targets, Ti content in the films decreases through life from 7 to 3.5 at%

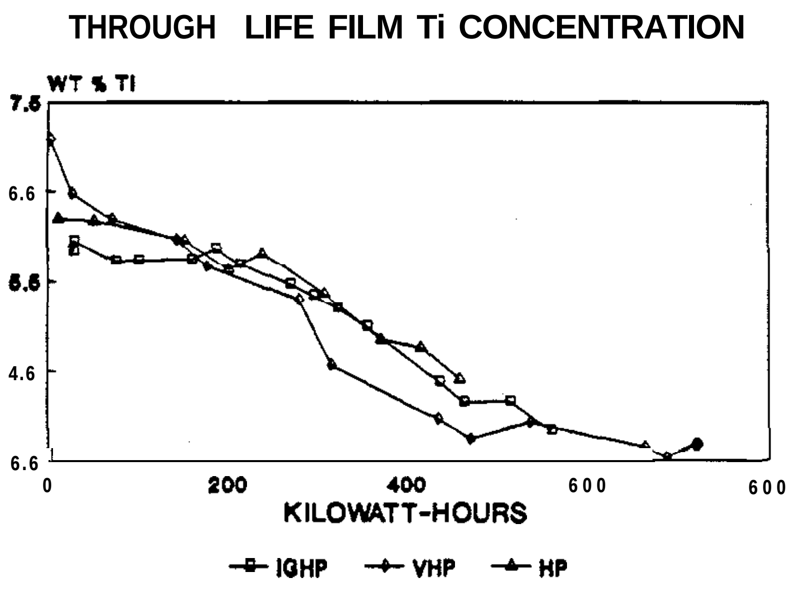

Figure 3. With the decrease in film Ti content, there is a corresponding decrease in the bulk film resistivity. When a full erosion zone RMX™ style target is employed, the fall-off in film resistivity is minimized.

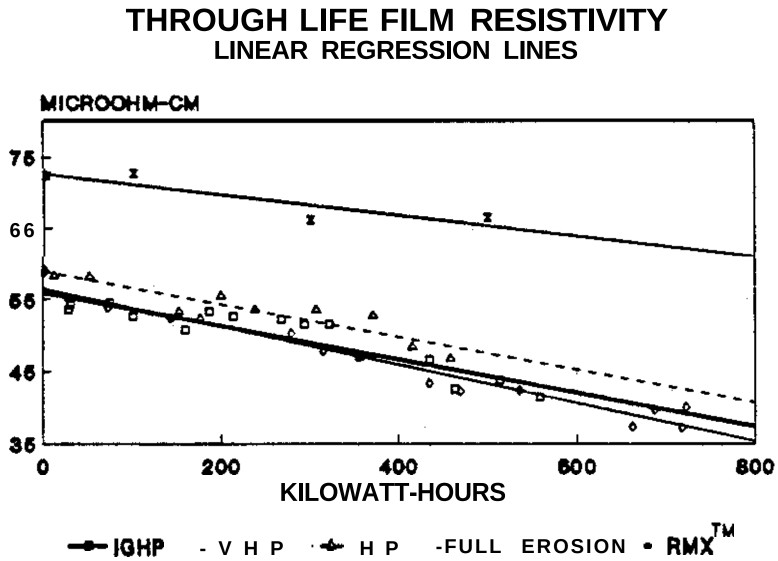

Figure 4. The reflectivity of all films was constant throughout target life.

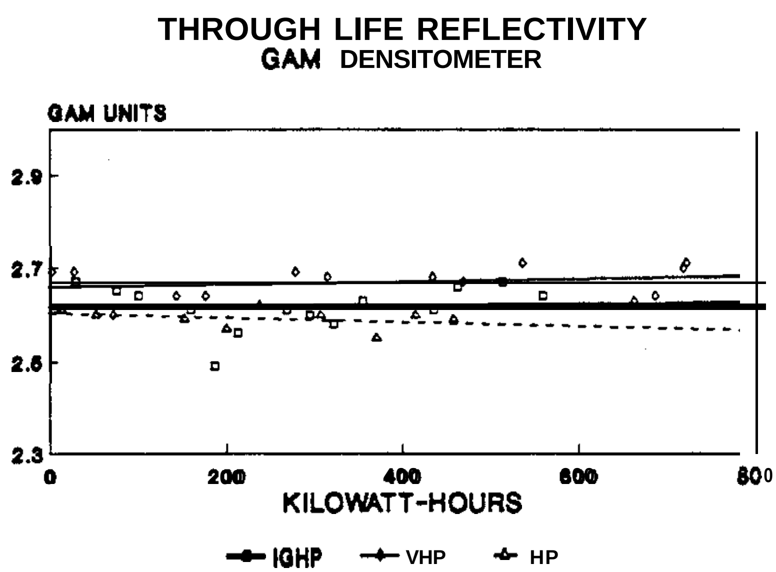

Figure 5. Ti - W phase diagram from Binary Alloy Phase Diagrams - Volume 3[5]

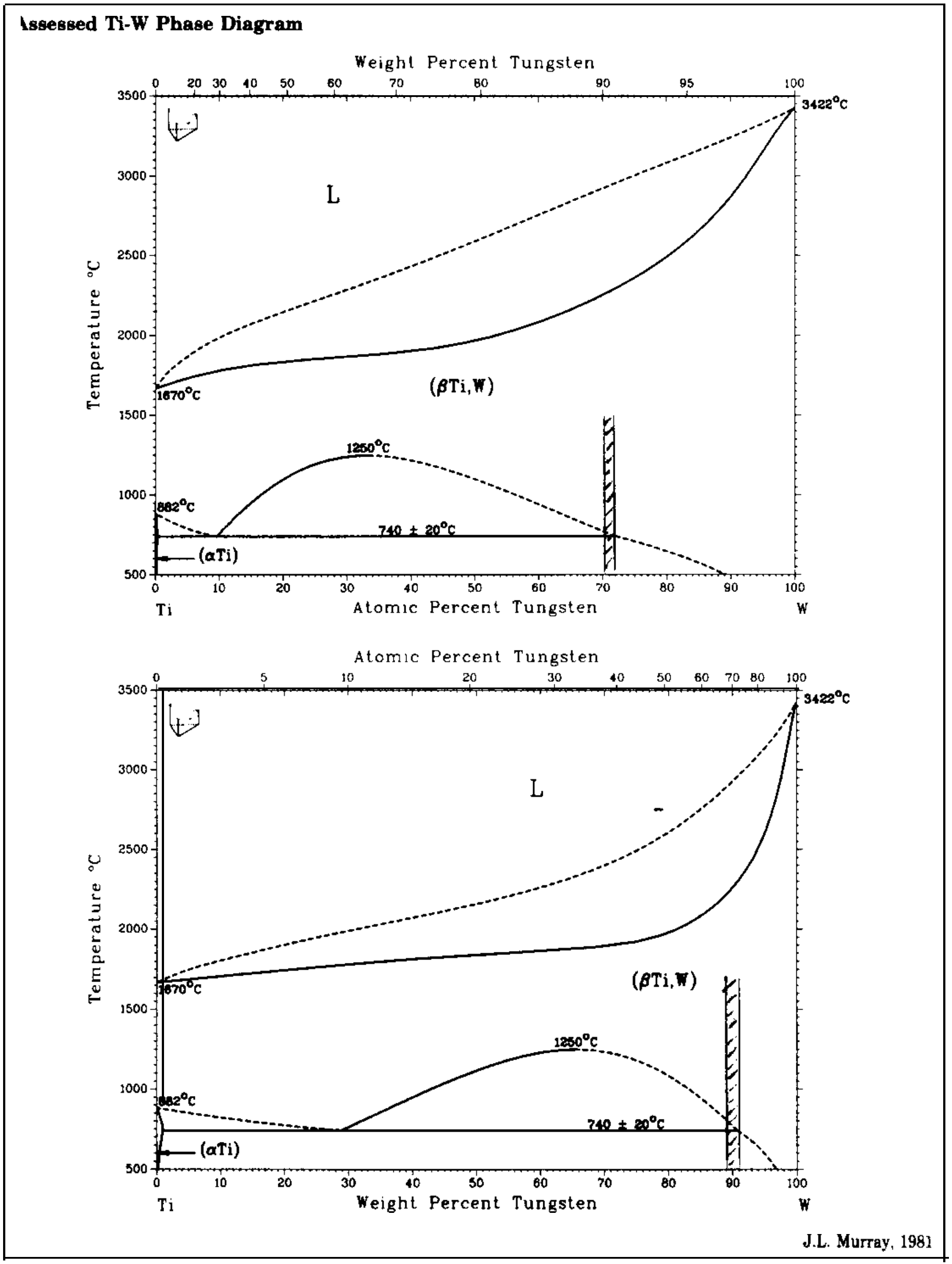

Figure 6a. **Microstructure of inert gas hot pressed Ti - W sputtering targets. The structure shows β- stablized Ti in a W rich matrix.**