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TUNGSTEN-TITANIUM SPUTTERING TARGET TECHNOLOGY

by

D. Udler, D. Marx Ph.D., G. Murphy
Materials Research Corporation
Advanced Materials Division

Summary-
Tungsten-Titanium, (W/Ti) alloys have been extensively used as diffusion barriers in interconnect metallization and are today the leading materials for this application. The purpose of this paper is to provide the user with insight into the metallurgy of W/Ti and to clarify some often misrepresented related concepts such as microstructure, grain size and spatial compositional uniformity.

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A Note About Materials Research Corporation...

MRC's first business activity was the production of high purity materials for research purposes. Today, MRC is recognized as the world leader in the production of both systems and materials for demanding, high-technology thin film applications including the manufacture of semiconductors, magnetic and optical storage discs, electronic displays, automotive sensors, and electronic circuitry.

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.

TUNGSTEN-TITANIUM SPUTTERING TARGET TECHNOLOGY

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Materials Research Corporation
Advanced Materials Division
Orangeburg, New York

1. INTRODUCTION

Tungsten-Titanium, (W/Ti) alloys have been extensively used as diffusion barriers in interconnect metallization and are today the leading materials for this application. Continuing device miniaturization imposes ever increasing demands for high quality sputtering targets yielding consistent, defect-free films throughout target life.

W/Ti targets were first commercialized by Materials Research Corporation in 1970. This development gained rapid acceptance as a significant improvement over the existing two-step process. Today MRC is the major supplier of a wide variety of target shapes and compositions suitable for all existing sputtering systems. The purpose of this paper is to provide the user with insight into the metallurgy of W/Ti and to clarify some often misinterpreted related concepts such as microstructure, grain size and spatial compositional uniformity.

2. TARGET QUALITY

The meaning of “high quality” with respect to W/Ti targets has been changing as the industry’s understanding of the complex correlations among target bulk properties, sputtering process parameters and deposited film characteristics has improved. Process parameters are defined by the target user as a function of a specific sputtering machine and deposition mode. Control of these parameters reduces the number of variables in the deposition process and provides more uniform and repeatable film properties. Through close cooperation with users, MRC has designed and optimized W/Ti targets that exhibit the following uniform properties from target to target:

- Microstructure
- U and Th content
- Dimension control
- Total -
- Alkali content
- Alloy composition
- Density
- Oxygen content

3. Review of Quality Parameters

3.1. MICROSTRUCTURES

The thermodynamic limitations imposed by the nature of the W/Ti matrix helps explain why the powder metallurgy manufacturing process is employed for this material. The equilibrium phase diagram for the W/Ti binary system is shown in Figure 1. At temperatures encountered in powder consolidation, tungsten and titanium exhibit unlimited mutual solubility, favoring the formation of a substitutional solid solution in adjacent particle contact areas.

Mutual solubility diminishes dramatically with decreasing temperatures. Upon cooling at about 100°C /hr, (typical in the manufacturing practice,) a target bulk structure consists of pure Ti and almost pure W„ with the latter containing a very minute amount of Ti still in solid solution. Concentration analysis by SEM confirms the dual-phase nature of the material (Figure 2).

Any high temperature method of blended powder consolidation, either pressure or pressureless (sintering), results in a two-phase microstructure composed of W-rich and Ti-rich particles alloyed at the inter-particle boundaries. Such a system, a mixture by definition, represents the only stable state predicted by equilibrium thermodynamics for W/Ti alloys at room temperature. Therefore, any claim to a solid solution alloy structure as opposed to a two-phase structure is invalid. All W/Ti powder metallurgical targets are two-phase alloys comprised of a mixture of W-rich and Ti-rich particles.

Another often misinterpreted microstructural parameter of W/Ti targets concerns average grain size. For pure metals or single phase alloys, the grain size is the length of an area with similar crystallographic orientation. These areas, called grains, are readily identifiable on a polished and etched cross-section by a network of grain boundaries separating the individual grains. An example of such a structure of pure P/M tungsten appears in Figure 3A.

The average grain size lies in the 10 to 30 micron range. In the most frequently used target alloys, 10 to 18 weight percent Ti corresponds with 32 to 57 volume percent. In these P/M alloys, grains of each metal, formed through coalescence of fine powder particles, cannot grow any further due to the restricting presence of other metal “islands”. At the end of the consolidation process, a target microstructure consists of pure Ti particles, ranging in size from 1 to about 30 microns, uniformly dispersed throughout a fine-grained (less than 5 microns) tungsten matrix. This structure is presented in Figure 3B. The photomicrograph shows that the largest structural elements are Ti (dark) particles.

Thus, assigning a single grain size to W/Ti alloys is not always accurate. The maximum size of the largest microstructural component, however, is an important feature for measurement and control of microstructural uniformity and mechanical stability. The MRC process assures that W/Ti targets will not have grains larger than 40 microns. Powder metallurgically fabricated W/Ti targets always possess an equiaxial, untextured structure. Textures (unidirectional, preferential arrangement of certain microstructural components or crystallographic planes) can be imposed by plastic deformation only (deposition processes and crystal growth are not considered here). None of the commonly used means of powder consolidation including inert gas hot press, hot isostatic press, cold press and vacuum sinter, or vacuum hot press involves plastic deformation of fully densified bulk material.

Although plastic deformation does occur during consolidation under external pressure, it is highly localized and is instantly released by neck growth, the leading mechanism of densification.

3.2. **Density**

Porosity is the single most important source of structural discontinuity in powder metallurgy parts. Eliminating it (or reducing it to the lowest level possible) is essential for proper sputtering target manufacture. Density, usually expressed as a percentage of the theoretical density, can be calculated by a mechanical mixture rule:

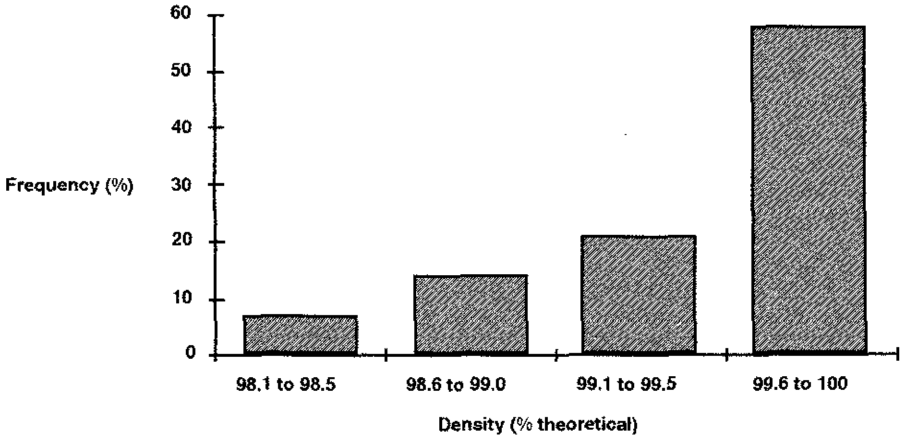
$$Dab = lOO/(wt\%A/Da + wt\%B/Db) \quad [g/cc]$$

Where: Dab = alloy theoretical density
wt%A,wt%B = weight percentage of components A and B
Da, Db = densities of pure metals A and B.

Theoretical room temperature densities of common target alloys are listed below: Beta-phase density, which occurs at elevated temperatures, is not an appropriate measurement.)

Wt% Ti	10	12	14	16	18
D (g/cc)	14.56	13.84	13.21	12.65	12.12

Consolidated blank and finish-machined target densities are constantly monitored as a part of MRC's in-process statistical process control (SPC) system. Statistical data for all W/Ti compositions and target shapes recently manufactured by MRC are tabulated below:



(x = 99.4 σ = .232)

Comprehensive evaluations of particulate generation vs. target bulk properties were conducted by MRC in cooperation with target users. Test results demonstrated that at density levels of 93 to 95% theoretical, the number of particles is a function of the oxygen content and is unaffected by residual porosity or powder consolidation method. In a cross section, dense material (as evaluated by the Archimedes principle) exhibits only a few micropores, as observed in figure 3C.

3.3. METALLIC IMPURITIES AND OXYGEN.

MRC manufactures three grades of W/Ti targets: ULTRA™, ULTRA 2™ and ECLIPSE™. Each has respectively higher levels of purity. The following table lists the specified minimum purity' for these grades:

	ULTRA	ULTRA 2	ECLIPSE
Metallic Purity	99.99%	99.995%	99.9975%
Min. Density (% theo)	95%	97%	97%

MRC employs advanced analytical capabilities to certify actual analytical data obtained from a sample of the fully consolidated target, as opposed to reporting only raw materials purity.

The most common film quality problems encountered in W/Ti sputtering are mobile ion (alkali) concentration, particulate generation, and gradually diminishing film resistivity (seen only in flat-style targets). Although all of these problems are to a great extent attributable to process parameters (cleanliness of the system, type of equipment and deposition mode), there is a well-established correlation between film and target properties.

Reduced alkali content directly improves CV shift. Figure 4 illustrates the results of the MRC-conducted CV shift testing. The data shows a linear correlation between total alkali (Na, K and Li) content and CV shift voltage. The Eclipse™ grade W/Ti, the purest in the industry, has been shown to exhibit a CV shift of only 8 millivolts.

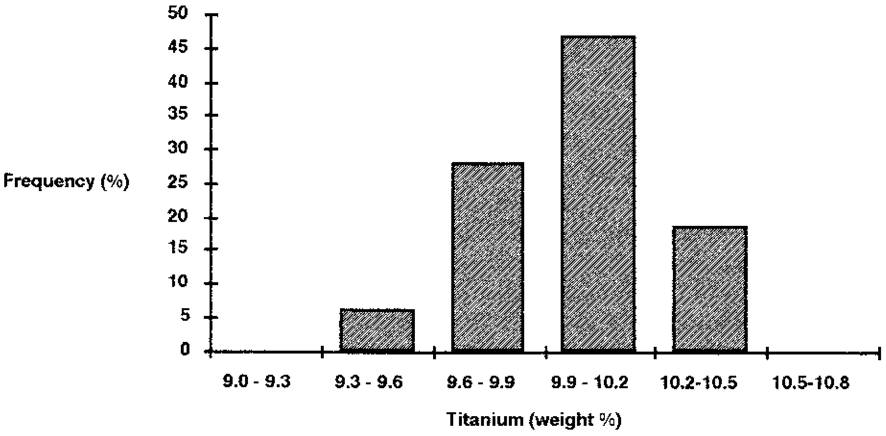
Figure 5 illustrates the results of a recently completed study comparing particulate generation from an MRC target with targets from two alternative sources. Data was collected over three months of actual wafer fab production. The data reveal that MRC's fully dense target consistently produced lower particulate counts than the two other suppliers' materials. This reduced particulate count has a positive impact on device yield.

Film resistivity measurement is the most convenient non-destructive means of evaluating the diffusion-resistant W/Ti layer. Consequently, it is widely employed in sputtering operation as an in-process QC evaluation. For non-reactive sputtering done in clean and well adjusted systems, resistivity is directly correlated with film Ti content as shown in Figure 6.

The deposited film is usually Ti deficient as compared with target bulk; i.e.: the ratio % Ti(film)/% Ti(target) is less than unity and falls in the 0.5 to 0.9 range, with a specific value being constant for a given system. This is due to a variety of factors, including the effects of Argon pressure on backscattering, the spacing between the target and the wafer, and the design of the target/cathode assembly. Problems arise when this ratio does not stay constant, and film resistivity gradually diminishes from wafer to wafer until the product is rendered unacceptable and the target must be removed.

Bulk composition of all targets is routinely checked as a part of MRC's standard SPC practices. In order to clarify the resistivity roll-off issue, spatial compositional uniformity within the targets has been evaluated for the most typical shapes (flat and conical). Both sets of data for the W/Ti 10 wt% alloy are presented below:

A. Statistics on bulk composition for W/lO%Ti-

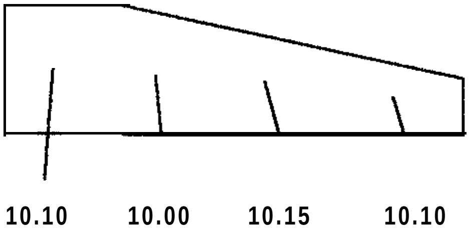


B. Spatial compositional distribution data (Titanium in weight %)

Flat target-

Edge	Middle	Edge
9.66	9.91	9.92
9.89	9.90	9.93
9.88	9.87	9.93

Conical target-



Emission spectroscopy, the most sensitive method of Ti evaluation in bulk alloy form, is accurate to approximately 0.1 wt % . Therefore, the above data would indicate analytical scatter rather than actual composition variation. It is unlikely that target non-uniformity accounts for this film resistivity roll-off phenomenon.

4. SUMMARY

This paper has provided clarification of some often misinterpreted concepts of W/Ti metallurgy. The microstructural evaluations of MRC-processed W/Ti targets reveal a thermodynamically stable material manufactured to high density, purity, and compositional tolerances. The consistency manufactured into these target materials provides users trouble-free operation, low particulate counts, and high purity (minimal C-V shift)

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[1] Materials Research Corporation certifies its tungsten/titanium product purity as the result of vigorously searching for a full range of commonly-occuring metallic element impurities in each production lot. This method of certification is much more stringent than that of some other suppliers, who have adopted the practice of searching for only a few "critical impurity" elements and stating a purity percentage which accounts for only these few impurities. It is MRC's belief that true material purity is properly stated only if the full range of commonly-occuring impurity elements is reported.

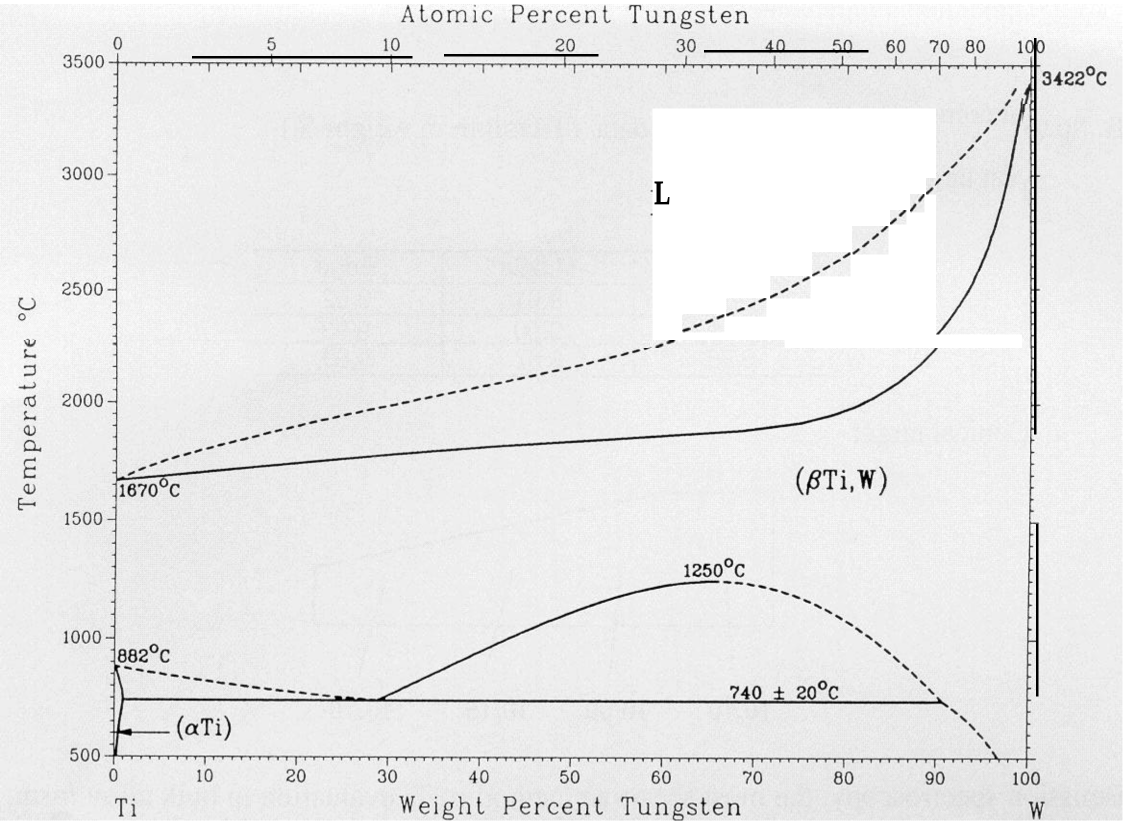

Figure 1- Tungsten-titanium phase diagram.

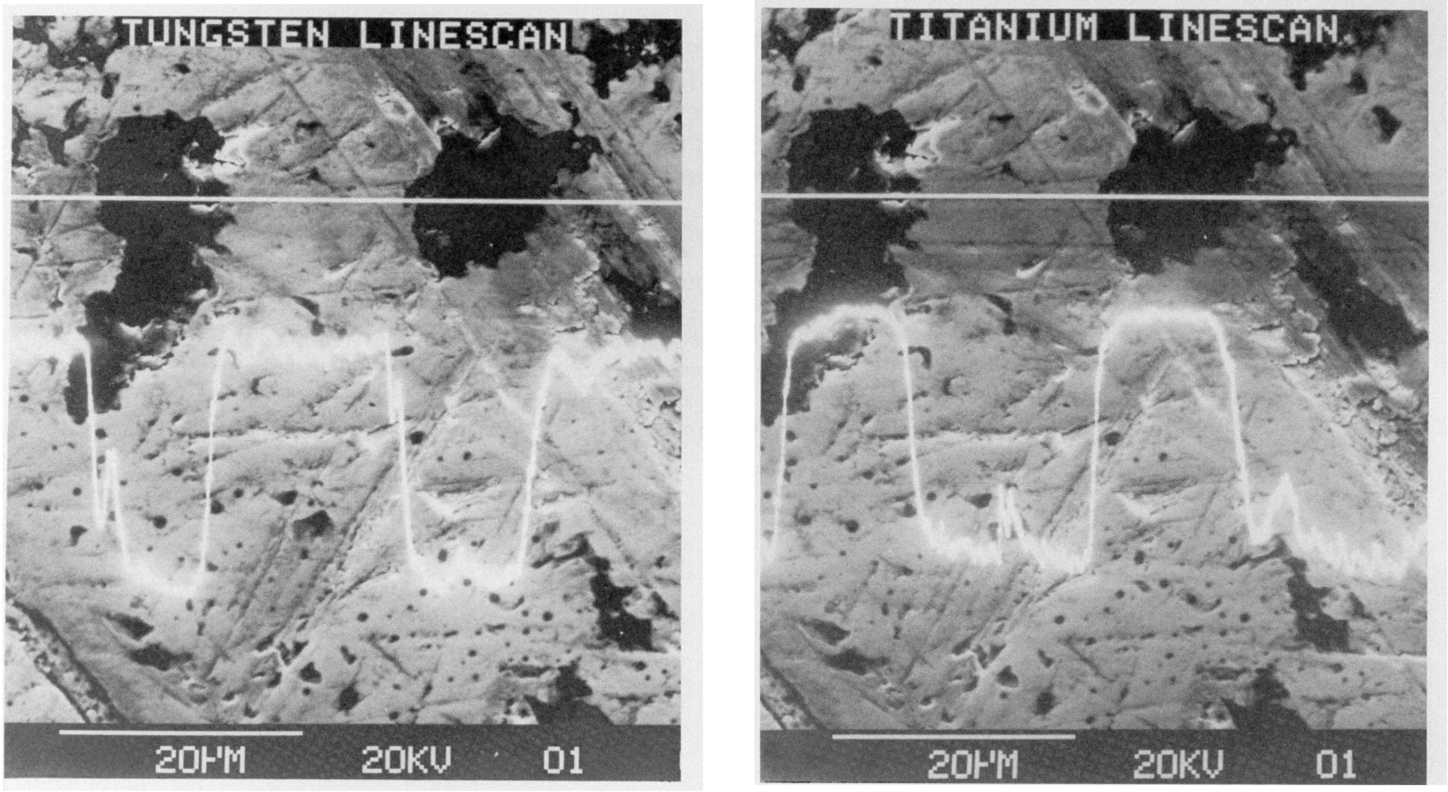

Figure 2- Concentration profiles in the W/Ti alloy.

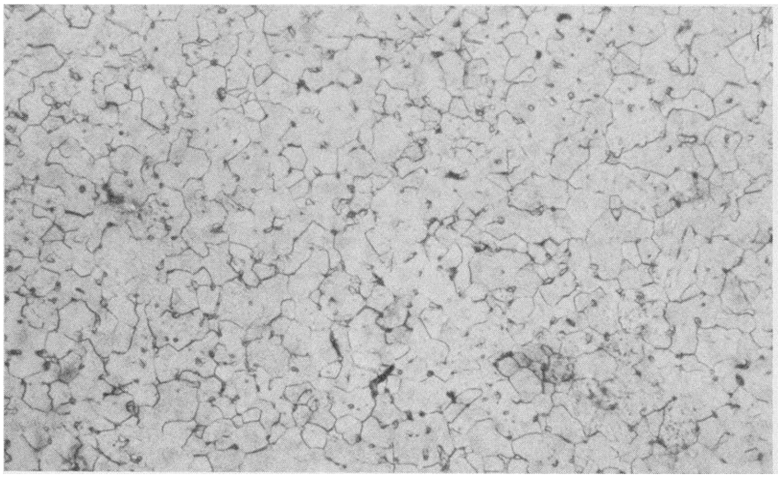

Figure 3A- Pure tungsten microstructure (400x).

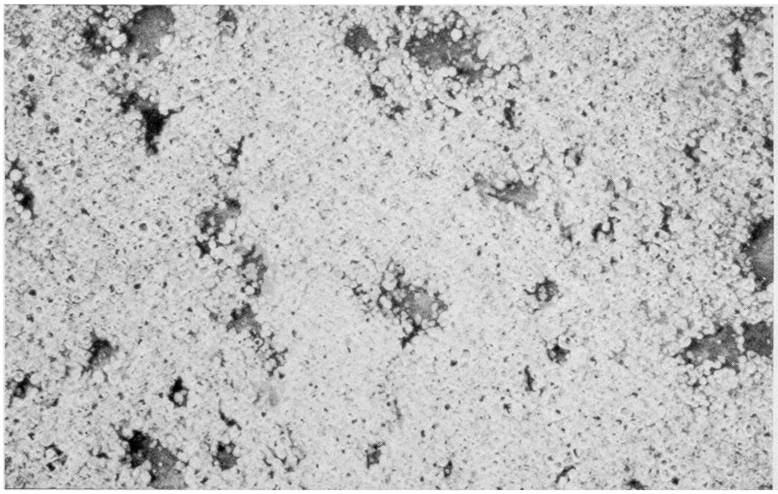

Figure 3B- W 10%Ti, etched (200x).

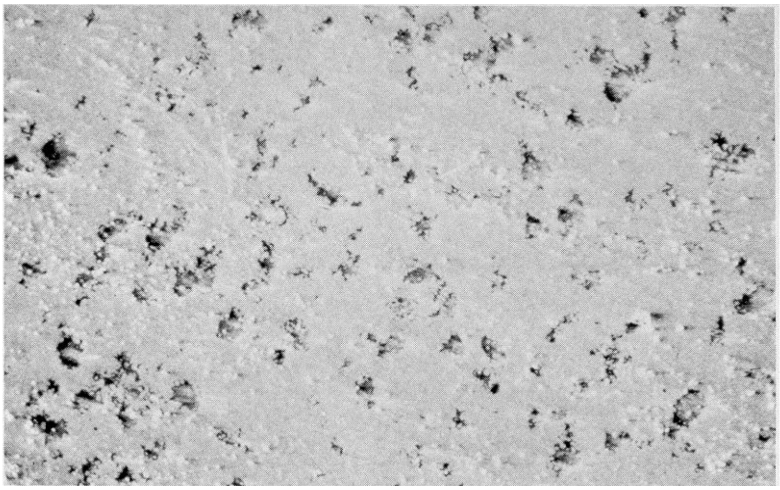

Figure 3C- W 10% Ti, polished (100x).

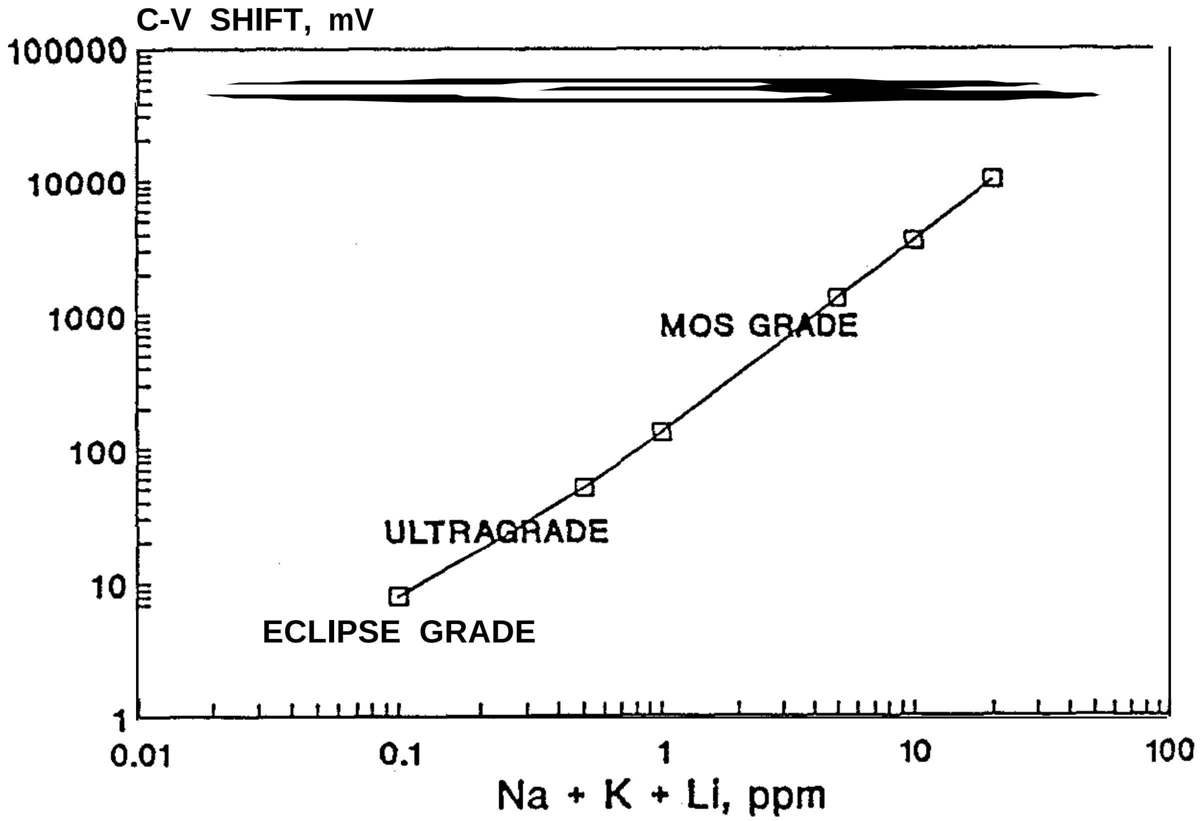

Figure 4- Target alkali content vs. C-V shift.

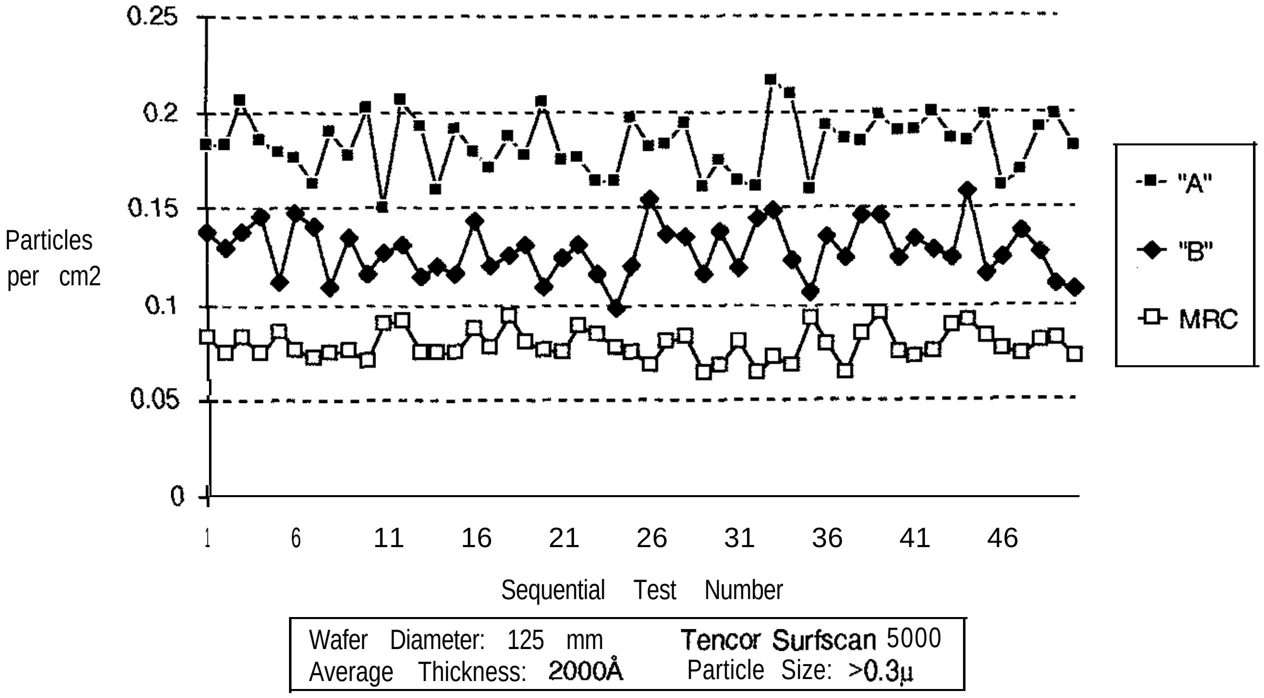

Figure 5- WTi particulate generation data.

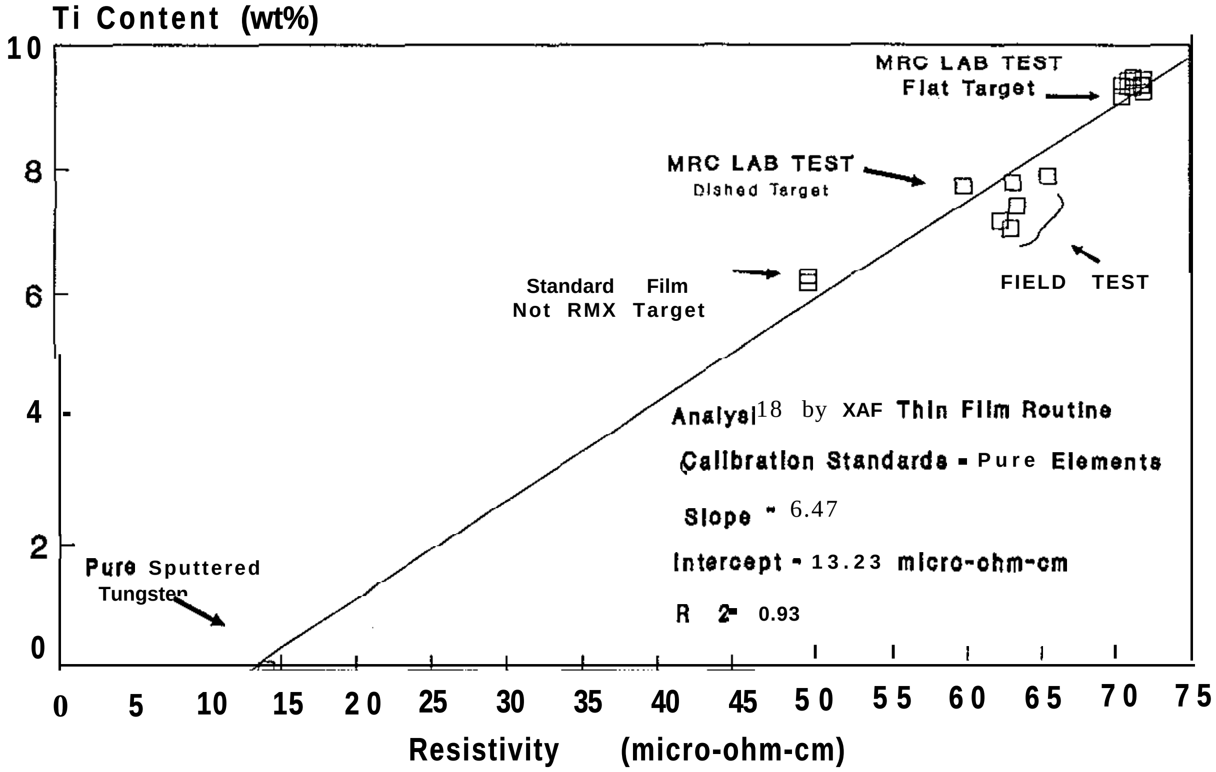

Figure 6- Film titanium content vs. resistivity.
(Target titanium content 10 %)

203.AMD.AG/PR.O196,1k

Materials
Research
Corporation

Advanced Materials Division
Orangeburg, New York 10962 USA
Phone (914) 359-4200 Fax (914) 359-3453