30
4-7-86 JS (1)

I - 25632

(2)

GEPP-TIS--892

DE86 008791

DF # 1641-1

CHARACTERIZATION OF THE IMPURITIES IN TUNGSTEN/SILICON-GERMANIUM CONTACTS

H. A. Gregg, Sr.
Chemistry Laboratory

March 26, 1986

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

General Electric Company
Neutron Devices Department
P. O. Box 2908
Largo, Florida 34294-2908

Prepared for the
U. S. Department of Energy
Albuquerque Operations Office
Under Contract No. DE-AC04-76DP00656

MASTER

EB

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

NOTICE

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by tradename, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
Price: Printed Copy \$5.00 ; Microfische \$3.50

ABSTRACT

Secondary ion mass spectrometry and Auger electron spectrometry depth profiling were used to determine impurity distributions in sputter deposited tungsten films over N-type and P-type 80/20 silicon-germanium elements of thermoelectric devices. These analyses showed that silicon, oxygen, sodium, boron, and phosphorus were present as impurities in the tungsten films. All these impurities except oxygen and sodium came from the substrate. Oxygen was getterred by the tungsten films, while sodium was possibly the result of sample handling.

Further, the results from this study indicate that an oxide build-up, primarily at the tungsten/silicon-germanium interface of the N-type material, is the major contributor to contact resistance in thermoelectric devices.

TABLE OF CONTENTS

Section	Page
INTRODUCTION	1
SAMPLE PREPARATION AND TESTING	2
Semiquantitative SIMS and AES Analyses	3
RESULTS	5
General Observations	5
Sodium	5
Silicon	5
Oxygen	5
Boron and Phosphorus	7
THE EFFECTS OF ANNEALING AND AGING ON SAMPLES	7
Influence of Oxygen	8
Segregation of Boron	8
Two Mechanisms for Contact Degredation	9
CONCLUSIONS	9
ACKNOWLEDGEMENT	10
REFERENCES	11
DISTRIBUTION	12

ILLUSTRATIONS

Number		Page
1	Thermopile Construction Showing Arrangement of Silicon-Germanium Elements and Tungsten Contacts After Sputter Deposition, Photoresist, and Etch Steps	1
2	Diagram of Sample Showing Area Where Tungsten Film Was Sputter Desposited for Analysis	2
3	Auger Depth Profile of Aged Tungsten Film Over N-Type Silicon-Germanium Thermopile Element Showing Oxygen in Tungsten Film and Build-Up at Interface	6

ILLUSTRATIONS (Continued)

Number		Page
4	Auger Depth Profile of Aged Tungsten Film Over P-Type Silicon-Germanium Thermopile Element Showing Oxygen in Tungsten Film	6

TABLES

Number		Page
1	Semiquantitative SIMS Data for Samples Exposed to Air Before Anneal	4
2	Semiquantitative SIMS Data for Samples Annealed In Situ	4

INTRODUCTION

The thermoelectric devices are currently used for constant low current power applications. These units provide electrical power through the use of the thermoelectric properties of the N-type and P-type silicon-germanium alloys. Throughout their use, thermoelectric units had problems with contact resistance at the tungsten/silicon-germanium interface; problems which eventually lead to electrical failure. The tungsten contacts electrically connect neighboring N-type and P-type silicon-germanium elements in the thermopile units (Figure 1). It has been found that the contact between the N-type silicon-germanium alloy and the sputter deposited tungsten film exhibits 90 to 95 percent of the contact resistance observed in failed high resistance units [1].

Figure 1. Thermopile Construction Showing Arrangement of Silicon-Germanium Elements and Tungsten Contacts After Sputter Deposition, Photoresist, and Etch Steps

This study was conducted to determine which impurities were responsible for the high contact resistance between the silicon-germanium elements and the sputter deposited tungsten contact material.

Secondary ion mass spectrometry (SIMS) depth profiling was used in this study to provide an effective analysis at parts per million levels of the impurities involved in contact failure modes. Although SIMS is not a quantitative technique, approximate concentration levels can be obtained through the use of relative ion yields (RIY) for the various elements.

SAMPLE PREPARATION AND TESTING

Samples were supplied by the Special Devices Development unit at the General Electric Neutron Devices Department (GEND). These samples consisted of sectioned units 6.5 mm long (see Figure 2) which had been polished* on one side, showing two wide channels (one N-type and one P-type) of the 80/20 silicon-germanium alloy. Polishing and sputtering parameters were essentially the same as in standard production. These samples will be designated by an "S" followed by the number of thermopiles with which they were processed, indicating sister samples. The samples were sputter deposited with tungsten for three hours at 31.8 to 32.1 torr argon pressure over an ascending substrate temperature range of 375 to 480°C to produce films 2.46 to 2.59 μm thick.

Figure 2. Diagram of Sample Showing Area Where Tungsten Film Was Sputter Deposited for Analysis

*Standard polishing to a 1- μm diamond finish used for thermopile ends prior to tungsten deposition.

After tungsten deposition, the samples followed two different process routes. Sample S402119 was removed from the vacuum following deposition before any annealing was done, while Sample S401120 was annealed in situ for two hours following deposition, then removed from the vacuum. Each sample received eight hours of annealing at 550°C in a Perkin-Elmer sputter deposition system prior to analysis. Following the eight-hour anneal, the samples were referenced "as deposited."

Samples were then analyzed using SIMS and Auger electron spectrometry (AES) depth profiling to determine trace and bulk elemental distribution both within the tungsten films and at the interface between the tungsten film and silicon-germanium substrate.

Following the first analysis series, these samples were each aged for seven hours at 630°C in a vacuum furnace. After aging, the samples were again analyzed by SIMS and AES depth profiling techniques.

SEMIQUANTITATIVE SIMS AND AES ANALYSES

SIMS and AES depth profiling were used in combination to determine the relative and semiquantitative distribution of elements within the tungsten films; therefore, data are listed in Tables 1 and 2 at approximate concentration levels.

The general behavior of both samples as deposited and after aging will be described, followed by specific results for N-channel characteristics, P-channel characteristics, and sample deviations for samples annealed in situ and samples exposed to air before annealing.

Table 1. Semiquantitative SIMS Data for Samples Exposed to Air Before Anneal

Sample Region	As Deposited				Aged			
	Na%	Si%	B	P	Na%	Si%	B	P
N-CHANNEL (Phosphorus)								
Surface	0.13	1.16	75 ppm	-	0.16	1.7	35 ppm	115 ppm
Near Interface	0.04	0.61	75 ppm	-	0.45	1.7	105 ppm	305 ppm
Tungsten Bulk	Oxygen (Auger)		1.2%		Oxygen (Auger)		2.1%	
P-CHANNEL (Boron)								
Surface	0.08	1.4	-	110 ppm	1.1	2.4	40 ppm	160 ppm
Near Interface	0.03	0.43	-	100 ppm	1.7	1.3	55 ppm	220 ppm
Tungsten Bulk	Oxygen (Auger)		2.6%		Oxygen (Auger)		2.0%	

Table 2. Semiquantitative SIMS Data for Samples Annealed In Situ

Sample Region	As Deposited				Aged			
	Na%	Si%	B	P	Na%	Si%	B	P
N-CHANNEL (Phosphorus)								
Surface	0.03	1.2	40 ppm	-	0.5	1.9	20 ppm	75 ppm
Near Interface	0.04	0.79	55 ppm	-	0.7	1.8	20 ppm	75 ppm
Tungsten Bulk	Oxygen (Auger)		1.3%		Oxygen (Auger)		1.1%	
P-CHANNEL (Boron)								
Surface	0.10	1.1	70 ppm	240 ppm	0.3	2.6	20 ppm	50 ppm
Near Interface	0.07	0.60	80 ppm	245 ppm	0.4	1.0	20 ppm	60 ppm
Tungsten Bulk	Oxygen (Auger)		1.8%		Oxygen (Auger)		1.0%	

RESULTS

GENERAL OBSERVATIONS

Sodium

In the as deposited tungsten films, evenly distributed sodium concentrations of 0.03 to 0.13 percent were observed. However, in the aged samples, the bulk sodium levels increased to 0.3 to 1.7 percent while the peak or maximum levels were seen in the tungsten near the Si/Ge interface. Diffusion of sodium from the silicon germanium into the tungsten films was indicated.

Silicon

In the as deposited samples, silicon showed a maximum at the surface of the tungsten in the range of 1.1 to 1.4 percent. These levels tapered off to 0.43 to 0.79 percent in the bulk near the SiGe interface. After aging, the silicon concentrations at the surface increased to 1.7 to 2.6 percent, while the bulk levels near the SiGe interface increased to 0.8 to 1.9 percent. This indicated a diffusion of silicon* through the tungsten film, with silicon dioxide formation as the probable driving force [2,3]. In addition, the P-channel silicon diffusion rate was nearly twice as fast as the N-channel diffusion rate, indicating the presence of a diffusion barrier or other diffusion inhibiting mechanism at the N-channel.

Oxygen

The oxygen levels, in general, were observed in the range of 1.2 to 2.6 percent within the bulk tungsten films. The as deposited samples showed an anomaly in that the tungsten bulk over the N-channels of each sample contained 0.5 to 1.4 percent less oxygen than that observed over the P-channels (possibly indicating depletion).

After aging, oxygen levels became evenly distributed throughout the tungsten films at 1 to 2 percent. However, the oxygen showed a build-up at the tungsten/silicon-germanium interface over the N-channels (Figure 3), which was not shown over the P-channels (Figure 4).

Comparing Sample S402119 with Sample S401120 (Tables 1 and 2), there was 0.5 to 1.0 percent more oxygen in the tungsten bulk of Sample S402119 which had been air-exposed before being annealed.

*Silicon is the primary diffusing specie in the formation of refractory metal silicides [4].

Figure 3. Auger Depth Profile of Aged Tungsten Film Over N-Type Silicon-Germanium Thermopile Element Showing Oxygen in Tungsten Film and Build-Up at Interface (in situ annealed sample)

Figure 4. Auger Depth Profile of Aged Tungsten Film Over P-Type Silicon-Germanium Thermopile Element Showing Oxygen in Tungsten Film (in situ annealed sample)

Boron and Phosphorus

Air Exposure Prior to Annealing

Sample S402119 had been exposed to air before annealing. The as deposited sample had boron and phosphorus concentrations of 50 to 100 ppm evenly distributed throughout the tungsten film. When the sample was aged, these impurities accumulated at higher concentrations of 50 to 300 ppm near the tungsten/silicon-germanium interfaces. This appeared more pronounced on the N-channel side.

In Situ Anneal Prior to Air Exposure

Sample S401120, as deposited, had been annealed in situ for two hours prior to exposure to air. Boron and phosphorus concentrations of 40 to 250 ppm were observed in the tungsten bulk with a moderate accumulation of each near the tungsten/silicon-germanium interface. This accumulation appeared more pronounced on the N-channel side. Since this condition did not occur in the as deposited Sample S402119, it is believed to be associated with the in situ anneal. The anneal had apparently diffused the oxygen, boron, and phosphorus to the interface.

The aged sample, Sample S401120, showed boron and phosphorus concentrations to be lower than the as deposited sample. These concentrations were evenly distributed at 10 to 100 ppm with no evidence of the previously described interface accumulation of impurities.

THE EFFECTS OF ANNEALING AND AGING ON SAMPLES

Silicon was observed in the as deposited tungsten films at 1.0 to 1.5 percent near the surfaces and 0.4 to 0.8 percent in the bulk near the interfaces. After aging, these levels increased to 1.7 to 2.6 percent at the tungsten surfaces and 0.8 to 1.9 percent in the bulk adjacent to the interfaces, indicating a net diffusion of silicon through the tungsten film with silica formation at the surface as the driving force.

It was also noted that the P-channel diffusion rate during aging was nearly twice as fast as the N-channel diffusion rate. This indicates the possibility of diffusion barrier formation at the N-channel/tungsten interface. Oxide formation at tungsten/silicon interfaces has been shown by other investigators [5] to prevent silicon diffusion and subsequent silicide formation. An oxygen build-up was observed at the N-channel interface (Figure 3) while a less significant amount of oxygen was observed at the P-channel interface (Figure 4) after aging.

Silicide formation [6] at the interface also occurs during the aging process, with more silicide forming over the P-channels. These films show a stress related failure mechanism (blistering) first at the P-type interface and then at the N-type after extended aging.

INFLUENCE OF OXYGEN

Oxygen is gettered in the bulk tungsten films at concentrations of 1 to 2 percent as shown by Auger analysis. Of all the contaminants, oxygen as the oxide layer has the most influence on intermetallic reactions and electrical functions at the interface and grain boundaries [7,8]. It has been found that annealing at elevated temperatures causes oxygen to readily diffuse out of the bulk tungsten to the interface forming silica [5,8]. Also, it has been proposed that a bulk percentage of oxygen (less than 1 percent) is sufficient to provide a monolayer of oxide surrounding each grain of tungsten in the bulk film and that these impurities can strongly influence film resistivities [9]. In addition, voids have been shown by transmission electron microscopy (TEM) [9] to exist for similarly sputter deposited tungsten silicide films constituting some 10 to 20 percent of the film volume.

The observation of less oxygen in the tungsten bulk over the N-channels of the as deposited samples may indicate that more oxygen is at that interface in the form of silica. This supports the proposed mechanism of an interfacial oxide causing resistance to increase until failure occurs [1].

Further support is given by the data which show a 0.5 to 1.0 percent increase in oxygen in the tungsten bulk of the sample which was exposed to air prior to the annealing step. Oxygen is obviously gettered quite readily by the loose, columnar grained tungsten films which have not been annealed or densified to seal or reduce grain boundaries. Annealing or aging serves to redistribute the available oxygen throughout the tungsten films, while simultaneously oxidizing available silicon at the tungsten grain boundaries or at the silicon-germanium interface. Annealing in situ would serve to densify the tungsten film and seal the outer surface grain boundaries of the tungsten films with silica or some other oxide, thus preventing, or at least inhibiting, oxygen penetration during subsequent air exposure.

SEGREGATION OF BORON

It should be noted that boron preferentially segregates into growing silica and silicide films while phosphorus is rejected by the oxide and will, in fact, accumulate in the substrate adjacent to the silica film [10,11]. It was observed in this study that both boron and phosphorus are found in the tungsten films sometimes at nearly dopant levels. The values for boron range from 5 to 80 ppm and 10 to 300 ppm for phosphorus. Dopant levels of boron are 420 ppm and for phosphorus are approximately 380 to 420 ppm in the silicon-germanium P-type and N-type elements respectively. Other work [1] has shown boron in the tungsten over the N-channel with a peak at the interface of 13 to 95 ppm, depending on the sample.

TWO MECHANISMS FOR CONTACT DEGRADATION

Two mechanisms may cause the contact degradation at the N-channel which accounts for 90 to 95 percent of the overall resistance found in the N-type and P-type contacts. Both mechanisms assume oxide formation with silicon oxidizing to silica.

The first mechanism would have the oxide forming at the tungsten/silicon-germanium interface with boron preferentially segregating into the oxide as mentioned earlier. This provides dual avenues of resistance: 1) Oxide formation would begin to insulate the contact interface [12], while 2) the boron concentration would shift the interface toward intrinsic behavior.

The second mechanism is essentially the same as the first except that the oxide formation would occur at the tungsten grain boundaries, virtually insulating each tungsten conductor grain in the film. Other investigators have calculated that the bulk percentage of oxygen required to provide monolayer coverage of each grain is less than approximately 1 percent [8,9].

CONCLUSIONS

The results of this study indicate that the thermopile may be electrically active at all times, specifically during tungsten deposition and other heating processes. Thus, oxygen with a very high electron affinity is attracted preferentially to the N-channels or N-type (electron donor) silicon germanium elements. This is specifically indicated by the following observations:

1. The depletion of oxygen in the as deposited tungsten bulk over the N-channels compared to P-channels indicates a pile-up of oxygen at the N-channel interface.
2. Boron segregation [1] to N-channel interfaces indicates an oxide formation [10] at the N-channel interface.
3. The P-channel diffusion rate for silicon in the tungsten film was nearly twice as fast as the N-channel rate, indicating a diffusion barrier formation at the N-channel interface such as silica [7,10].
4. Depth profile data (Figures 3 and 4) for aged samples show a build-up of oxygen at the tungsten/silicon-germanium N-channel interface.

This explains why the N-channel is responsible for 90 to 95 percent [1] of the contact resistance value seen in the thermopiles. This phenomenon would not occur at the P-channel since the primary charge carriers there are holes, and would reject electronegative oxygen. With this constraint in mind, the N-channel would degrade through the first mechanism mentioned earlier, while the P-channel might follow the second mechanism to a slower resistance build-up.

These analyses show that the resistance problem associated with the tungsten/silicon-germanium interface may be reduced with adequate control of oxygen at the interface. It is known that a thin oxide film promotes good adhesion of the tungsten film while minimizing silicide formation and blistering after extended aging. However, more than a few monolayers of oxide [6] will cause the contact resistance to be too high for efficient operation of the thermopile.

The data show that sputtered tungsten films have a significant amount of oxygen (1 to 2 percent) associated with them. It appears that the tungsten film getters oxygen from a vacuum or readily from air, and that subsequent heating processes diffuse the oxygen to the silicon-germanium interface. The interfacial contamination seems to be controllable by using in situ annealing after sputtering. This annealing process inhibits the oxygen gettering/diffusing phenomena.

Another way to exclude or reduce oxygen interference would be to produce a more dense film. Very dense films have been applied to thermopiles using chemical vapor deposition (CVD). The aging characteristics [1] as well as the adhesion properties of the CVD films have been excellent. This method warrants serious consideration if consistent high reliability films are desired for thermoelectric devices.

ACKNOWLEDGEMENT

The author expresses thanks and appreciation to R. A. Rossmeisl, W. D. Carter, and G. Moore who provided valuable technical information and assistance for this study.

REFERENCES

1. R. A. Rossmeisl, GEND (1984), unpublished.
2. M. Y. Tsai, H. H. Chao, L. M. Ephrath, B. L. Crowder, A. Cramer, R. S. Bennet, C. J. Lucchese, and M. R. Wordeman, J. Electrochem. Soc. 128, 2207 (1981).
3. S. Zirinsky, N. Hammer, F. M. d'Heurle and J. J. Baglin, Appl. Phys. Lett., 33, 76 (1978).
4. R. D. Thompson and K. N. Tu, Thin Solid Films, 93, 265 (1982).
5. D. J. Silversmith, D. D. Rathman and R. W. Mountain, Thin Solid Films 93, 413 (1984).
6. H. A. Gregg, Sr. and G. Moore, GEND (1985), to be published.
7. S. P. Murarka, J. Vac. Sci. Technol. B 2 [4], 693 (1984).
8. C. B. Cooper III, R. A. Powell and R. Chow, J. Vac. Sci. Technol. B 2 [4], 718 (1984).
9. D. R. Campbell, S. Mader and W. K. Chu, Thin Solid Films, 93, 341 (1984).
10. E. Morgan, T-Y. J. Chen, D. A. Reed and J. E. Baer, J. Vac. Sci. Technol. A, Vol. 2, No. 3, 1266 (1984).
11. F. Jähnel, J. Biersack, B. L. Crowder, F. M. D'Heurle, D. Fink, R. D. Issac, C. J. Lucchese, and C. S. Peterson, J. Appl. Phys. 53, 3059 (1982).
12. P. E. Schmid, P. S. Ho, and T. Y. Tan, J. Vac. Sci. Technol., 20 (3), 688 (1982).

DISTRIBUTION

DOE

E. E. Patenaude, PA0
OSTI, Oak Ridge (30)

GE

Technical Information Exchange,
Schenectady (5)

GEND

W. C. Brown	055
R. W. Bruner	055
W. D. Carter	055
C. C. Eichman	055
H. A. Gregg, Sr.	021
D. J. Malbrough	030
G. Moore	031
W. C. Pijawka	001
J. L. Provo	030

Technical Information Center (5) 018
Specialist-Technical Publications 018
(5 + Reproduction Masters)
4699C/0116D