1995

Oxidation behavior of RF sputter deposited zirconium diboride thin films

Xiaonong Zou
San Jose State University

Follow this and additional works at: https://scholarworks.sjsu.edu/etd_theses

Recommended Citation

Zou, Xiaonong, "Oxidation behavior of RF sputter deposited zirconium diboride thin films" (1995). *Master's Theses*. 1195.

DOI: <https://doi.org/10.31979/etd.dz9t-pubk>
https://scholarworks.sjsu.edu/etd_theses/1195

This Thesis is brought to you for free and open access by the Master's Theses and Graduate Research at SJSU ScholarWorks. It has been accepted for inclusion in Master's Theses by an authorized administrator of SJSU ScholarWorks. For more information, please contact scholarworks@sjsu.edu.

INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

UMI

A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
313/761-4700 800/521-0600

**OXIDATION BEHAVIOR OF
RF SPUTTER DEPOSITED ZIRCONIUM DIBORIDE THIN FILMS**

A Thesis

Presented to

The Faculty of the Department of Materials Engineering

San Jose State University

In Partial Fulfillment

of the Requirements for the Degree of

Master of Science

By

Xiaonong Zou

August 1995

UMI Number: 1377286

UMI Microform 1377286

Copyright 1996, by UMI Company. All rights reserved.

**This microform edition is protected against unauthorized
copying under Title 17, United States Code.**

UMI

**300 North Zeeb Road
Ann Arbor, MI 48103**

© 1995

Xiaonong Zou

ALL RIGHTS RESERVED

APPROVED FOR THE DEPARTMENT OF MATERIALS
ENGINEERING

Dr. Guna Selvadurai

Dr. Peter Gwozdz

Mr. Jeffrey Bull

APPROVED FOR THE UNIVERSITY

ABSTRACT

Oxidation Behavior of RF Sputter Deposited ZrB₂ Thin Films

By

Xiaonong Zou

The ZrB₂ thin films were RF sputter deposited onto silicon wafers and characterized in terms of microstructures, stoichiometry, and adhesion strength. The oxidation behavior of the films was then investigated gravimetrically. The experimental data showed that the oxidation of the ZrB₂ thin films followed a parabolic relationship, and was diffusion limited. Applying ZrB₂ thin films on the silicon surface reduced oxidation rates significantly. The sputtered films exhibited a columnar structure and had good adhesion on the silicon.

ACKNOWLEDGMENTS

I wish to express my sincere gratitude to my thesis advisor Dr. Guna Selvaduray, Professor, Materials Engineering Department, for his valuable guidance, assistance, and suggestions throughout my thesis research and write-up, and also for his encouragement and advice during my graduate study. I also wish to extend my appreciation to Mr. Jeffrey Bull of NASA-Ames, and Dr. Peter Gwozdz of the College of Engineering, San Jose State University, for their assistance and advice as members of the thesis committee.

Special thanks are given to Mr. Giorgio Riga of Riga Analytical Laboratories for kindly doing the AES analysis on the sputtered samples.

My deepest gratitude goes to my parents for their continued encouragement and financial support of my graduate study.

TABLE OF CONTENTS

	Page
ABSTRACT	iv
ACKNOWLEDGEMENTS	v
TABLE OF CONTENTS	vi
LIST OF TABLES	xi
LIST OF FIGURES	x
 Chapter	
1. Introduction	1
2. Literature review	3
2.1 Oxidation of metals	3
2.1.1 Metal oxidation mechanism	3
2.1.2 Oxide growth-induced stresses	6
2.1.3 Oxide kinetics of metals	11
2.2 Oxidation behavior of ZrB_2	15
2.2.1 Thermodynamic considerations	15
2.2.2 Oxidation kinetics of ZrB_2	18

2.3 Properties of ZrB_2 , ZrO_2 and B_2O_3	23
2.3.1 Properties and structure of ZrB_2	23
2.3.2 Structure and properties of ZrO_2	26
2.3.3 Properties of B_2O_3	30
2.4 R.f. sputter deposition	32
3. Experimental procedures	36
3.1 Objective	36
3.2 Equipment and materials	36
3.2.1 Equipment	36
3.2.2 Materials	39
3.3 Deposition rate calibration	39
3.4 Deposition of ZrB_2	40
3.5 Characterization of the sputtered films	41
3.5.1 Microstructure and composition of the films	41
3.5.2 Thin film adhesion test	42
3.6 Oxidation test	43
3.6.1 Oxidation of ZrB_2	43
3.6.2 Pre-oxidation of ZrB_2 thin films	46
3.6.3 Thermal cycling test	47

4. Results and discussion	49
4.1 Deposition rates	49
4.2 Characteristics of the films	54
4.2.1 Scanning electron microscopy of the sputtered film	54
4.2.2 Chemical composition of the as-sputtered films	59
4.2.3 Adhesion strength of the films	62
4.3 Oxidation behavior of the sputtered films	63
4.4 Micrography of pre-oxidized samples	66
4.5 Results from cyclic oxidation exposure	70
5. Conclusion	77
6. References	79
7. Appendix	83
A. Data from oxidation test	83
B. Calculation of standard free energy of formation for ZrB_2 and ZrO_2	87
C. Result from adhesion test	89
D. Calculation of P-B ratio for ZrB_2	90

LIST OF TABLES

	Page
Table 1. Pilling-Bedworth ratios for a number of metals	9
Table 2. The oxygen partial pressure for the oxidation of ZrB_2 at different temperatures	19
Table 3. Properties of ZrB_2	24
Table 4. Important properties of ZrO_2	28
Table 5. Deposition parameters for the silicon wafers	41
Table 6. Summary of specimen characteristics used in oxidation test	47
Table 7. Summary of optimal deposition condition	53

LIST OF FIGURES

Figure	Page
1. Schematic representation of processes that are involved in the gaseous oxidation at a metal surface	5
2. Break down of oxide films	7
3. Diffusion coefficients of ions in some common ceramics	12
4. Standard free energy of formation of B_2O_3 , ZrB_2 and ZrO_2 , as well as other oxides at different temperatures	17
5. Oxidation of ZrB_2	21
6. Schematic of MB_2	25
7. Phase diagram of zirconium-boron system	27
8. Fluorite structure	29
9. Vapor pressure of B_2O_3 as a function of temperature	31
10. Schematic representation of a glow discharge structure	33
11. Flow chart of experimental procedures	37
12. Schematic diagram of r. f. sputtering system used in the experiment	38
13. The test stud assembly	44
14. Adhesion test using Seabastian Five multi-purpose tester	45

15. Deposition rate as a function of argon pressure	50
16. Influence of r. f. power on deposition rate	52
17. SEM picture of as-sputtered film surface	55
18. Cross-section of as-sputtered film	56
19. Zone model of sputtered films	58
20. Energy dispersive spectrum of as-sputtered film	60
21. AES of as-sputtered films	61
22. Oxidation kinetics of r. f. sputtered ZrB_2 films	64
23. SEM picture of sputtered films after 192 hours exposure at 1200 °C	65
24. SEM picture of sputtered films pre-oxidized at 400°C	67
25. SEM picture of sputtered films pre-oxidized at 600 °C	68
26. SEM picture of sputtered films pre-oxidized at 900 °C	69
27. Comparison of oxidation rates of bare silicon, ZrB_2 -coated silicon, and silicon with pre-oxidized ZrB_2 coatings	71
28. SEM picture of bare silicon after 192 hours exposure at 1200°C	73
29. SEM picture of ZrB_2 -coated silicon after 192 hours exposure at 1200°C	74
30. SEM picture of silicon with pre-oxidized ZrB_2 coating after 192 hours exposure at 1200°C	75

1. Introduction

Zirconium diboride (ZrB_2) is a refractory compound having excellent characteristics such as extreme hardness, good wear and abrasion resistance, high chemical stability against corrosion or attack by molten salts and metals, and good oxidation stability. Zirconium diboride also has the lowest bulk electrical resistivity among various metal borides and high thermoionic emission. Accordingly, ZrB_2 is a potential candidate for applications such as protective coatings against wear, abrasion and corrosion, for electrical contacts in semiconductor device fabrication, and for use as a photothermal solar absorber.⁽¹⁾

ZrB_2 has been used in several high temperature applications, including leading edges and nose cones of hypersonic re-entry vehicles, rocket nozzles and air augmented components.⁽²⁾ These applications are mainly based on the good oxidation resistance of ZrB_2 at high temperatures. W. C. Tripp and H. C. Graham, who conducted a study on the oxidation of bulk zirconium diboride, reported that ZrB_2 oxidizes stoichiometrically and its oxidation kinetics follows parabolic time dependence.⁽³⁾ However, there has been limited investigation of the oxidation behavior of zirconium diboride thin films. This research was therefore undertaken to investigate the oxidation of zirconium diboride thin films and the potential use of zirconium diboride thin films as a protective coating against high temperature oxidation.

D.c. sputtering, r.f. sputtering and chemical vapor deposition have been used to deposit ZrB_2 films onto substrates.^(4, 5, 6) All the films

obtained by these methods were reported as being hard and adherent. However, r.f. sputtering provides a direct and simple way to deposit ZrB_2 thin films, while avoiding the surface charge of d.c. sputtering and chemical handling problems associated with chemical vapor deposition. In this investigation, zirconium diboride thin films were deposited onto silicon wafers by r.f. sputtering. After deposition, the thin films of zirconium diboride were evaluated in terms of surface topography, chemical composition and adhesion strength. The oxidation experiments were carried out by exposing the samples to oxidizing atmospheres at a given temperature, and monitoring their weight change. These experiments allowed the evaluation of the amount of oxides formed. The time dependence of the extent of oxidation was also determined.

The background literature pertaining to this research is reviewed in Chapter Two. Chapter Three presents the experimental procedures, and Chapter Four contains the experimental results, including the analysis and discussion of the results obtained. The conclusions from this investigation are presented in Chapter Five.

2. Theory and Literature Review

The oxidation behavior of zirconium diboride in gaseous atmosphere, especially air, is similar to that of metals. Oxidation of either zirconium diboride or metals results in the formation of an oxide scale on the surface. This phenomenon is frequently termed scaling, or dry oxidation. Because metal oxidation has been studied extensively, and its results can provide a basis for understanding the oxidation of zirconium diboride, this review begins with possible mechanisms for the formation of oxide layers on the metal, the types of oxide layers that can form, and the kinetics of oxide formation on metals. The oxidation behavior of zirconium diboride is then discussed from the chemical thermodynamics and kinetics perspectives. Due to the fact that the physical and chemical properties of the oxidation products are important, since they may both influence the subsequent rate of reaction, the properties of materials that are involved in the oxidation of zirconium diboride are also reviewed. The physics of r.f. sputtering is presented at the end of the review.

2.1 Oxidation of metals

2.1.1 Metal oxidation mechanism

When a metal oxidizes, there is a change in the free energy of the system. It is this change that is the “driving force” of the reaction. If the standard Gibb’s free energy of the oxide phase is lower than the sum of the standard Gibb’s free energies of the metal and oxygen, the metal tends to form oxides in air or in aqueous solutions, even at room temperature. In the case of the formation of an oxide layer on a metal, where the oxygen partial

pressure is $P_{O_2}^g$, the effective oxygen partial pressure at the oxide-metal interface, $P_{O_2}^i$, is determined by the temperature and the standard Gibb's free energy of the oxidation reaction, ΔG_f° , as shown by Equations [1] and [2].

$$(P_{O_2}^i)^{1/2} = e^{\Delta G_f^\circ / RT} \quad [2]$$

If the oxygen partial pressure in the atmosphere ($P_{O_2}^g$) is greater than $P_{O_2}^i$, oxidation will occur spontaneously.

The process of metal oxidation is one in which a metal combines with an atom or molecule of a reactant and loses electrons. The oxygen concentration gradient (chemical potential) across the oxide layer provides the driving force for oxygen diffusion toward the metal-oxide interface. A gradient of the chemical potential of the metal ion in the opposite direction produces metal-ion diffusion toward the oxygen atmosphere.

A schematic representation of this metal-oxide-gas reaction is shown in Figure 1. The oxidation reaction occurs at the metal-oxide interface, leading to the formation of metal ions. Meanwhile, the reduction takes place at the oxide-gas interface, resulting in the production of oxygen ions. For the oxide layer to increase in thickness, it is necessary that electrons be conducted to the oxide-gas interface, where the reduction occurs. M^{2+} ions must diffuse away from the metal-oxide interface, and /or O^{2-} ions must diffuse toward this same interface. The oxide layer here may serve as a

Figure 1. Schematic representation of processes that are involved in the gaseous oxidation at a metal surface ⁽⁷⁾

barrier for preventing the metal from further oxidation. The reason for this is that once the surface of a metal begins to oxidize, subsequent oxidation can take place only when oxygen ions diffuse through the oxide layer and react with the metal ions at the metal-oxide interface, or when metal ions diffuse through the oxide layer and react with oxygen ions at the oxide-oxidant interface. As the oxide layer thickness increases, the diffusion distance increases and the rate of oxidation decreases.

2.1.2 Oxide growth-induced stresses

Not all metal oxide scales can function as good barriers for curbing the metal substrate from further oxidation. This is due to the fact that the stresses developed during oxide layer growth may be great enough to lead to various modes of oxide damage, such as cracking or partly lifting away from the metal, so that the barrier between the metal and oxide does not become any more effective as oxidation proceeds. If the volume of the oxide is much less than that of the material from which it is formed, it will crack to relieve the strain. On the other hand, if the volume of the oxide is much greater, the oxide will tend to release the strain energy by breaking the adhesion between the metal and oxide, and springing away. Figure 2 shows how this can happen.

Hence, in order to be protective, the volume difference between the substrate and its oxide scale should be minimal. Pilling and Bedworth suggested that the ability of an oxide layer to protect the metal from further oxidation is related to the relative volumes of the oxide and metal.⁽⁸⁾ The

Figure 2. Breakdown of oxide films

ratio of these volumes, termed the Pilling- Bedworth (P-B) ratio, is determined from the following expression:

$$\text{P-B ratio} = A_{\text{O}}\rho_{\text{M}}/ A_{\text{M}}\rho_{\text{O}} \quad [3]$$

where A_{O} is the molecular weight of the oxide, A_{M} is the atomic weight of the metal, and ρ_{M} and ρ_{O} are the metal and oxide densities, respectively. For metals having a P-B ratio less than unity, the oxide film tends to be porous and unprotective because it is insufficient to fully cover the metal surface. If the ratio is greater than unity, there are compressive stresses in the film as it forms. For a ratio greater than between 2 to 3, the oxide scale may crack and flake off, continually exposing a fresh and unprotected metal surface. The ideal P-B ratio for the formation of a protective oxide film is slightly greater than unity. Table 1 lists the P-B ratios for some metals.⁽⁹⁾

From the P-B ratio, it can be expected that the oxide scales of Al, Mn, Ni, Co and Zr form very good protective layers. The P-B ratios of these metals shown in Table 1 are between 1 and 2. In practice, the addition of these elements will form a more adherent and protective oxide scale by virtue of producing a more favorable Pilling-Bedworth ratio. The zirconia based duplex thermal barrier coating (TBC) system used on gas turbines is an example of this application.⁽¹⁰⁾ The duplex TBC system consists of a thermal insulating CaO stabilized ZrO_2 top coat over critical superalloy components. An intermediate MCrAlY (M indicates Ni, Co, Fe, or their combinations) bond coat is applied before overlaying of the top coat to protect the substrate from high temperature oxidation by forming their

Table 1. Pilling-Bedworth Ratios for a Number of Metals

Metal	P/B Ratio
Al	1.28
Si	2.27
Mn	1.79
Zr	1.40
Cr	1.99
Co	1.99
Nb	2.61
Mg	0.81
Ta	2.33
Ni	1.52

protective oxide scales. The stabilized ZrO_2 top coat is the thermal protection coating.

From the Pilling-Bedworth ratios in the table, it would also be expected that the oxide scale on the Si surface is vulnerable to cracking because it has P-B ratio of 2.27.

Besides oxide growth-induced stresses, the oxide layer is also subjected to thermal stresses caused by thermal expansion differences between the oxide and the substrate. The thermal stress experienced by the oxide due to thermal expansion mismatch can be determined from Equation [4]:

$$\sigma = \Delta\alpha \cdot \Delta T \cdot E_o / (1 - \mu_o) \quad [4]^{(11)}$$

where E_o and μ_o are the elastic modulus and Poisson ratio of the oxide, respectively, $\Delta\alpha$ is the difference in linear thermal expansion coefficients between the oxide and substrate material, and ΔT is the difference between final temperature and initial temperature. In order to minimize the thermal stress imposed on the oxide scale due to thermal expansion mismatch at a given temperature difference, $\Delta\alpha$, μ_o and E_o must be minimized.

If the summation of all stresses exceeds some critical value, oxide scale failure occurs. These stresses include growth-induced stresses, thermally induced stresses and directly applied stresses. The onset of scale failure will change the oxidation behavior of the substrate metal. In the

following section, the relationship between oxidation kinetics of the metal and its oxide scale type is discussed.

2.1.3 Oxidation kinetics of metals

Oxidation kinetics are determined by the reaction mechanism, which, in turn, is determined by the properties of the reaction products. It should therefore be possible to predict these kinetics from the appropriate properties of the oxide, or conversely, predict these properties from the kinetics.

When the oxide that forms is nonporous and adheres to the metal surface, metal and oxygen migration across a reaction product layer become the determining factor of the rate of oxide layer growth. Hence, the oxide thickness, which changes with time, can be determined from the flux of the atomic and electronic species. The result yields a form of the parabolic rate law:⁽¹²⁾

$$dx/dt = K/x \quad [5]$$

Here, x is the oxide thickness at time t , and K is the parabolic oxidation rate constant directly related to the mobility, or diffusivities, of the electrically charged migrating species. The diffusion coefficients of ionic species in some common oxides are shown in Figure 3.⁽¹³⁾ It can be seen from Figure 3 that diffusion coefficients increase exponentially with temperature. If the oxide that forms has a very high melting temperature and low

Fig.3 Diffusion coefficients of ions in some common ceramics

diffusivity of the cationic and anionic species, then the oxidation rate can be expected to be low.

Lattice diffusion is assumed to be the rate determining transport process at high temperatures. The mechanism of scale growth at temperatures less than one half of the melting temperature of the oxide phase is determined by short-circuit diffusion of reactants through the oxide scale via point, line and boundary defects, even when the reaction kinetics are approximately parabolic.⁽¹⁴⁾

Parabolic oxidation is observed for metals when their oxide layers are coherent and ion diffusion is the rate-limiting process. However, linear and logarithmic oxidation are also observed. When the oxide scale is porous or flakes off (for P-B ratios less than 1 or greater than about 2), the transport of ions is more rapid than the chemical reaction involved in the oxidation step. As a result, the reaction becomes rate-limiting, leading to a diffusion-independent oxidation rate. The cracked oxide scale allows the oxidizing atmosphere to remain in contact with the metal and maintain a constant oxidation rate. The linear oxidation rate expression is :

$$x = At \quad [6]^{(15)}$$

where A is the temperature-dependent rate constant.

Examples of metals that display linear oxidation are Mg, Nb and Ta. Both Nb and Ta have P-B ratios greater than 2 and form oxide scales that

continually fracture during growth. The P-B ratio of Mg is less than 1, and thus MgO on Mg is a porous oxide scale.

Logarithmic oxidation takes the form:

$$x = A_1 \log (A_2 t + A_3) \quad [7]^{(16)}$$

where A_1 , A_2 and A_3 are rate constants. This type of oxidation occurs with very thin oxide scales (generally less than 100 nm) at low temperatures. For most oxidation reactions, an electrical potential of approximately 1V exists between the cathodic and anodic reaction areas. This electrical field causes the ions to diffuse when the oxide scale is very thin. As the oxide thickness increases, the effect of the electrical field diminishes and growth stops, except when the temperature is raised high enough to promote thermally activated diffusion. Metals like Al and Cu both show logarithmic oxidation at low temperatures with a limiting oxide thickness of ≈ 40 angstrom.

It can be seen from what has been discussed that the oxide scale type can be known by monitoring the oxidation kinetics. The onset of linear kinetics implies oxide scale failure, while parabolic kinetics indicates that the oxide scale formed on the metal surface is adhesive and continuous. The latter is a diffusion-controlled process. Its oxidation rate is greatly influenced by ionic mobility. High temperature enhances ionic mobility and thus increases the oxidation rate. Microstructural defects like dislocations and grain boundaries in the oxides act as short-circuit diffusion

paths and increase the oxidation rate .

Therefore, for an oxide scale to perform as an oxidation barrier, it must possess the following characteristics:

1. It must have a high melting temperature.
2. It must have a P-B ratio slightly above 1 so that the growth induced stress is low.
3. Its linear thermal expansion coefficient must be close to that of the metal on which the oxide scale is formed in order to minimize the thermal stress imposed on the oxide scale.
4. It must have good mechanical strength.
5. It must be thermodynamically stable.

Although ZrB_2 is a ceramic compound, and oxidation of ZrB_2 is more complex than what happens in the case of metals, the results obtained from the discussion of metal oxidation can be extended to the oxidation of ZrB_2 .

2.2 Oxidation behavior of zirconium diboride

2.2.1 Thermodynamic considerations

The oxidation of zirconium diboride produces zirconium dioxide and boron trioxide. The chemical reaction describing the oxidation of ZrB_2 is given in Equation [8].

The tendency of Reaction [8] to proceed forward is determined by the standard Gibb's free energy change, ΔG_R^0 , that would accompany it. ΔG_R^0 , at the temperature of interest, can be calculated from the following:

$$\Delta G_R^0 = (G_{f, \text{ZrO}_2}^0 + G_{f, \text{B}_2\text{O}_3}^0) - (G_{f, \text{ZrB}_2}^0) \quad [9]$$

The standard Gibb's free energy of formation of ZrB_2 , B_2O_3 , and ZrO_2 over the temperature range of 300K to 1100K were calculated, and the plotted results are shown in Figure 4. It is apparent from Figure 4 that the standard Gibb's free energy of formation of both ZrO_2 and B_2O_3 are much more negative than that of ZrB_2 . Thus, the oxidation of ZrB_2 is thermodynamically favorable. The highly negative values of the standard Gibb's free energy of formation of ZrO_2 and B_2O_3 are indicative of their chemical stability.

The standard Gibb's free energy change of Reaction [8], ΔG_R^0 , is related to the equilibrium constant, K_p , by Equations [10] and [11].

$$\Delta G_R^0 = -RT \ln K_p \quad [10]$$

$$K_p = 1 / (p_{\text{O}_2})^{5/2} \quad [11]$$

where p_{O_2} is the equilibrium oxygen partial pressure, and R is the universal gas constant.

Fig. 4 Standard free energy of formation of B_2O_3 , ZrB_2 and ZrO_2

Based on Equations [10] and [11], the equilibrium oxygen partial pressure as a function of temperatures can be determined, as shown in Equation [12].

$$p_{O_2} = \exp (2/5 \Delta G_R^0 / RT) \quad [12]$$

The calculated values for p_{O_2} in the temperature range of 298 to 1100K are tabulated in Table 2. It can be seen from Table 2 that the threshold oxygen partial pressure required for the oxidation of zirconium diboride increases with increasing temperature, but is significantly lower than the partial pressure of oxygen in the atmosphere. This indicates that ZrB_2 is virtually guaranteed to be oxidized, and its oxide remains stable in atmosphere.

2.2.2 Oxidation kinetics of ZrB_2

The oxidation of ZrB_2 results in a weight increase. The weight increase is due to the incorporation of oxygen into ZrB_2 . Since ZrB_2 is oxidized stoichiometrically, the amount of oxygen incorporated into ZrB_2 (i.e. the amount of weight increase) can be converted to the amount of oxides that have been formed. Assuming the weight increase is Δm , the amount of ZrO_2 formed, m_{ZrO_2} , can be determined from Equation [13].

$$m_{ZrO_2} = \Delta m \times (M_{ZrO_2}) / 5 M_O \quad [13]$$

**Table 2 The oxygen partial pressure for the oxidation of ZrB_2
at different temperatures**

Temperature (K)	Partial oxygen pressure (atm)
280	1.01×10^{-145}
300	5.34×10^{-136}
400	6.80×10^{-100}
500	1.39×10^{-78}
600	3.04×10^{-64}
700	5.12×10^{-54}
800	2.43×10^{-46}
900	1.85×10^{-40}
1000	9.01×10^{-36}
1100	5.92×10^{-32}

The amount of B_2O_3 formed, $m_{B_2O_3}$, is given by Equation [14]:

$$m_{B_2O_3} = \Delta m \times (M_{B_2O_3} / 5 M_O) \quad [14]$$

M_{ZrO_2} and $M_{B_2O_3}$ are the molecular weights of ZrO_2 and B_2O_3 respectively. M_O is the atomic weight of oxygen.

Because of the strong intermetallic bonding in ZrB_2 and relatively small oxygen diameter, the oxidation of ZrB_2 can be assumed to proceed mainly by the diffusion of oxygen through the oxide layer to the ZrB_2 - oxide interface, where the oxidation reaction takes place. During the course of the oxidation process, the ZrB_2 - oxide interface moves into the ZrB_2 , as illustrated schematically in Figure 5.

The oxidation behavior of ZrB_2 thin films has been investigated by a limited number of researchers. E. Randich and D. D. Aured studied the application of ZrB_2 thin films as a selective solar absorber.⁽¹⁸⁾ They reported that the oxidation behavior of ZrB_2 had two distinct temperature domains: the temperature region below $597^\circ C$ and the temperature region above $652^\circ C$. Below $597^\circ C$, the measured weight gain was slow. In the low temperature range, an amorphous protective oxide was formed. In the high temperature range a crystalline and less-protective oxide was formed.

The oxidation behavior of ZrB_2 was also studied by J.J. Funngon and R. A. Lux.⁽¹⁹⁾ Their data also indicated that two distinct oxidation regions

Fig. 5 Oxidation of ZrB_2

existed. One region, at temperatures of 625 °C or lower, produced thin, “tarnish-like” oxide layers less than 100 nm in thickness, when oxidized for 256 minutes. The oxides developed on ZrB₂ at temperatures higher than 625 °C were significantly different, with these oxides attaining thicknesses of greater than 1 µm at 675 °C in dry oxygen in 60 minutes. They reported that both the thin and thick oxides developed with a parabolic dependence on oxidation time and were, therefore, diffusion limited.

Both studies showed that the oxidation rates of ZrB₂ increased dramatically at temperatures around 600°C, which divided the oxidation domains into two temperature regions; this was caused by the fact that an amorphous protective oxide was formed at low temperatures. The diffusion of oxygen through the amorphous oxide layer is much slower than through the crystalline oxide layer which formed at temperatures higher than 600°C. The increasing oxidation rate may also be due to the melting of B₂O₃ at about 500°C. This could also increase diffusivity of oxygen in the oxide layers.

These studies also suggested that oxide films developed on ZrB₂ surfaces were insulative and protective. Thus, pre-oxidizing as-sputtered ZrB₂ films in a controlled manner may be expected to increase the oxidation resistance of as-sputtered films.

2.3 Properties of ZrB_2 , ZrO_2 , and B_2O_3

As mentioned earlier, oxidation kinetics are determined by the reaction mechanism, which, in turn, is determined by the properties of the materials involved in the reaction. The oxidation of ZrB_2 results in the formation of ZrO_2 and B_2O_3 . The properties of these materials are important for understanding the oxidation behavior of ZrB_2 . Thus, their properties are reviewed in the following sections.

2.3.1 Properties and structure of zirconium diboride

Zirconium diboride is a microcrystalline gray powder having the composition of ZrB_2 . Table 3 lists some properties of ZrB_2 , and it can be seen that ZrB_2 has a very high melting temperature, and high hardness. It can also be seen from Table 3 that the coefficient of thermal expansion of ZrB_2 is $6.73 \times 10^{-6} \text{ cm/cm}^\circ\text{C}$, which is close to that of silicon ($3 \times 10^{-6} \text{ cm/cm}^\circ\text{C}$).

Zirconium diboride is a member of the MB_2 group, which has a two-dimensional network structure. The crystal structure of MB_2 was described by Roy M. Adam,⁽²¹⁾ and a schematic diagram of this structure is shown in Figure 6. The unit cell of MB_2 is hexagonal, and there is one formula weight per unit cell. The metal and the boron atoms are arranged in alternate planar hexagonal layers perpendicular to the c axis. The two-dimensional network structure favors properties such as high melting temperature, high hardness values, and high electrical conductivity.

Table 3. Properties of ZrB₂ ⁽²¹⁾

Melting temperature	2960°C
Coefficient of thermal expansion	6.73×10^{-6} cm/cm °C
Thermal conductivity	134 w/m k
Density	6.02 g/cm ³
Electrical resistivity	9.2×10^{-6} ohm cm
Tensile strength	241 MPa
Hardness	87-89 Rockwell A
Young's modules	440×10^9 Pa

Fig. 6 Schematic of MB_2 structure

Most diborides are very stable phases.

From the phase diagram of the zirconium-boron system, shown in Figure 7, it can be seen that ZrB_2 is a compound containing 19.1 wt% boron.⁽²²⁾ The phase region is very narrow, and thus zirconium diboride can be considered a line compound. Its melting temperature is about 3000°C.

2.3.2 Structure and properties of ZrO_2

ZrO_2 has very a high melting point and possesses good thermal and mechanical properties. The important properties of ZrO_2 are shown in Table 4. Since the P-B ratio of Zr is 1.4, a ZrO_2 oxide scale can be expected to be nonporous and adherent. The thermal conductivity of ZrO_2 is low, making it a good thermal insulator. Because of these properties, ZrO_2 has found applications as thermal protection coatings.

The P-B ratio of ZrB_2 to ZrO_2 , as calculated from Equation 3, is 1.05. Thus, a ZrO_2 oxide layer on the ZrB_2 surface can also be expected to be protective.

ZrO_2 exists in two crystallographic forms. The stable form of ZrO_2 at room temperature is the monoclinic fluorite structure, as shown in Figure 8. The unit cell is based on the face-centered cubic packing of the cations. There are four valence bonds to each oxygen ion. A notable feature of this structure is the large void in the center of the unit cell. ZrO_2 has a monoclinic-tetragonal transition at about 1000°C. The transition is a

Fig. 7 Phase diagram of zirconium-boron system

Table 4. Important Properties of ZrO₂ ⁽²³⁾

Melting point, °C	2715
Density, g/cm ³	5.56
Electrical resistivity, ohm cm	2300
Thermal conductivity at 100 °C, W/m K	1.95
Thermal conductivity at 1200 °C, W/m K	2.39
Thermal expansion coefficient at 300 °C cm/cm 10 ⁻⁶ /°C	7.2
Thermal expansion coefficient at 1200 °C cm/cm 10 ⁻⁶ /°C	10.8
Compressive strength at 25 °C, MPa	2058.00
Compressive strength at 1000 °C, MPa	1173.06
Tensile strength at 25 °C, MPa	137.20
Tensile strength at 1000 °C, MPa	101.53
Modulus of normal elasticity at 25 °C, GPa	185.35
P-B ratio	1.4
Modulus of normal elasticity at 1000 °C, GPa	126.51

Fig. 8 Fluorite structure⁽²⁴⁾

displacive transformation, requiring no thermally-activated diffusion. The large hysteresis in the transformation temperature is attributed to the large difference in specific volume of the phases, and results in cracking. This phenomenon should be taken into consideration during its application. Addition of CaO to ZrO₂ forms cubic solid solution, which has no phase transition, is one method of stabilizing zirconia.

2.3.3 Properties of B₂O₃

The other oxidation product of ZrB₂ is B₂O₃, which liquefies at temperatures higher than 450^oC. However, whether it vaporizes or not is dependent on three main factors: vapor pressure, temperature and atmospheric pressure. If the atmospheric pressure is greater than the vapor pressure at a given temperature, the liquid is still a stable phase and vaporization does not occur. The vapor pressure of B₂O₃ at different temperatures obeys the following relationship:

$$\log(p) = 11.748 - 16960/T \quad [15]^{(25)}$$

The vapor pressure of B₂O₃, as a function of temperature, is plotted in Figure 9, where the horizontal line represents atmospheric pressure. It can be seen that the vapor pressure of B₂O₃ does not exceed atmospheric pressure until 2500K.

Fig. 9 Vapor pressure of B₂O₃ as a function of temperature

2.4 R.f. sputter deposition

Although ZrB_2 has a relatively high electrical conductivity, and d.c. sputtering of it has been reported, the presence of oxides on the surface of ZrB_2 sputter targets prior to sputtering could cause positive charge accumulation and make d.c. sputtering difficult, due to the low electrical conductivity of the oxides. In addition to oxide formation, pores in the hot pressed ZrB_2 could also reduce the electrical conductivity. Thus, r.f. sputtering is better suited for deposition of ZrB_2 than d.c sputtering. Because r.f. sputtering was used for the deposition in this study, the basic physics of r.f. sputtering is reviewed here very briefly.

In r.f. sputtering, glow discharge processes are driven by high frequency power supplies, usually in the megahertz range. In such a system, there is no real cathode or anode so that the positive charge accumulation during one-half cycle can be neutralized by electron bombardment during the next half-cycle. Thus, r.f. discharge overcomes the typical problem associated with d.c. sputtering, i.e. the positive charging on the insulator surface, which results in extinguishment of the discharge.

The ability to sustain a stable glow discharge in a sputter system is influenced by the electrical conductivity of the target material, the argon pressure and the distance between target and substrate. This can be explained by the discharge structure, which is shown in Figure 10.⁽²⁶⁾ The most important region in this structure is the cathode dark space, i.e.

Fig.10 Schematic representation of a glow discharge structure

(a) Structure of a glow discharge

(b) Charged particle concentration in a glow discharge

(c) Voltage variation in a dc glow discharge

Crooks' dark space, between the negative glow and the cathode. The greatest part of the voltage drop between the anode and cathode occurs across the Crooks' dark space, and therefore charged particles experience their largest acceleration in this region. The reduced luminosity of the dark space is caused by this effect. Because electrons in the dark space are strongly accelerated and traverse through the space quickly, the electron density at any instant in the dark space is drastically reduced. Although there are fewer electrons, those present can gain high energies from acceleration by the electrical field. When they collide with gas atoms in the dark space, they are more likely to cause ionization, rather than excitation. As a result, fewer light-generating electron-atom collisions occur than in the negative and positive glow regions. Upon colliding with atoms in the dark space, electrons cause ionization and are also slowed. Therefore, the edge of the negative glow region provides an indication of where such slowed electrons start to be created in large numbers. If the pressure in the tube is reduced, the distance that the emitted electrons travel before colliding and becoming slowed becomes longer. Consequently, the dark space lengthens. If the pressure becomes too low, the dark space extends the full length between the electrodes, and the glow discharge is extinguished.

In summary, ZrB_2 , which is a refractory material, has a high melting temperature and can be expected to have good oxidation resistance. The main contributing factor towards its oxidation resistance is that oxides formed on the surface of ZrB_2 are protective and stable. Applying ZrB_2 films onto substrates could protect substrate materials from oxidation. This

investigation was designed to study the oxidation kinetics of ZrB_2 films at high temperatures, and from the results to evaluate the possibility of using such films to protect substrates from oxidation.

3. Experimental Procedures

3.1 Objective

The objective of this investigation was to study the oxidation behavior of ZrB_2 thin films at high temperatures, and evaluate the potential use of ZrB_2 thin films as protection layers to increase the oxidation resistance of the substrate materials. Based on the objective, the experimental procedures, summarized in the flowchart in Figure 11, were designed.

3.2 Equipment and materials

3.2.1 Equipment

R.F. sputter deposition was used for depositing ZrB_2 thin films in this investigation. It was chosen largely because r. f. sputtering avoids accumulation of positive ions on the ZrB_2 surface during the sputtering process. A schematic diagram of the r.f. sputter deposition system used in this investigation is shown in Figure 12. The system consisted of four main components: chamber, vacuum pumping system, matching box and r.f. generator. There were a substrate holder and a target plate inside the chamber. The substrate holder was grounded, and the substrate to be deposited was placed on it. The substrate temperature was measured with a chromel-alumel thermocouple. The material to be sputtered was placed on the target plate, which was connected to the r.f. generator through a

Fig.11 Flow chart of experimental procedures

Fig.12 Schematic diagram of r.f. sputtering system used in the experiment

matching box and biased to a negative potential. Cooling water was run through the plate during sputtering to cool the target material. The distance between target and substrate was 3 cm. The chamber was first pumped down to the 10^{-6} Torr base operating pressure by a mechanical pump and a turbo molecular pump sequentially. Then argon gas was introduced into the chamber through the gas purifier. The argon purity after running through the purifier was 99.99%. Ar was first brought in rapidly until the plasma was initiated. Then the argon pressure was regulated to the desired value. The chamber pressure was adjusted through a needle valve, and measured by both a thermogauge and a cold cathode gauge. The cold cathode gauge was used to measure pressures lower than 10^{-3} Torr.

3.2.2 Materials

The ZrB_2 target used for sputtering was purchased from Cerac Corporation and had a radius of 1.5 inch. It was hot pressed and had 95% theoretical density and a purity of 99.6%. The substrate material used for deposition rate evaluation was microglass slides. The substrates used for studying ZrB_2 thin film oxidation behavior were 1 inch diameter silicon wafers with (111) orientation.

3.3 Deposition rate calibration

The r.f. deposition rate is strongly influenced by argon pressure and input power when the distance between the substrate and the target is constant. For this reason, the deposition rates of the r.f. sputter system

under different argon pressures and different power levels were calibrated so that an optimal deposition condition could be determined. Microglass slides were used as substrates in this experiment.

A glass slide was cleaned with acetone and DI water. It was then partially covered with an electrical tape. The glass slide was deposited with ZrB_2 for 1.5 hours. Removal of the electrical tape after deposition left a step on the glass slide. The film thickness was measured using a Tencor α -step profiler. The deposition rate was then determined from:

$$\text{Rate} = \text{Thickness/deposition time} \quad [16]$$

The system deposition rates were determined for input power levels from 180 watts to 800 watts, at 100 watt increments, while the argon pressure was maintained at 50×10^{-3} Torr. Deposition rates were also determined for argon pressure increases from 40×10^{-3} Torr to 75×10^{-3} Torr, at a constant input power of 300 watts.

3.4 Deposition of ZrB_2 onto wafers

Based on the results from the deposition rate calibration, the optimal deposition parameters summarized in Table 5 were determined. These parameters were used for deposition onto silicon wafers. The wafers were both-side polished so that both sides had the same thermal, mechanical and chemical conditions.

Deposition was done on one wafer at a time. Deposition was first done on one side for 90 minutes; then the wafer was turned over and deposition carried out for the same length of time. The wafer was immersed in the stable, dark-pink colored plasma during deposition. The edge of the dark space was located in the middle of the target and substrate. The substrate temperature was 250°C. After deposition, the deposited wafers were kept in a desiccator. The film thickness was obtained by multiplying the deposition rate by the deposition time.

Table 5. Deposition parameters for the silicon wafers

Target material	ZrB ₂
Target-substrate distance	3 cm
RF input power	800 W
Working gas	99.99% Ar
Base pressure	6 x 10 ⁻⁶ torr
Gas pressure	50x10 ⁻³ Torrs

3.5 Characterization of the sputtered films

3.5.1 Microstructure and composition of the films

A Hitachi S520 scanning electron microscope (SEM) was used to characterize the film surface and cross-sections of the films obtained by sectioning a deposited wafer into two halves. All the samples for scanning electron microscopy were coated with approximately 250 angstroms of gold

film to prevent surface charging during electron beam bombardment. The films were examined for evidence of cracking, surface roughness, and grain structures. The films were also analyzed qualitatively with the Kevex-3000 energy dispersive spectroscope attached to the SEM, to identify the elements present in the sputtered films. The accelerating voltages used ranged from 20 kev to 25 kev.

The stoichiometry of the sputtered films was determined through Auger Electron Spectroscopy (AES) at Riga Analytical Laboratories. The AES analysis was performed after 200 angstroms of the film surface were sputter etched in situ.

3.5.2 Thin film adhesion test

The adhesion strength of the sputtered films was measured by a pull test. A Seabastian Five multi-purpose tester was used to perform the testing. Three silicon wafers deposited with 1 μm ZrB_2 films were tested. The average adhesion value from these samples was taken as the film adhesion strength.

A test stud pre-coated with adhesive was bonded to each film surface. The stud had a diameter of 0.141 inch. The adhesion strength between the stud and adhesive was 7500 psi. The back of the wafer was bonded to an aluminum supporting plate. The stud, wafer and supporting plate were held together in contact using a spring mounting clip to form a test stud assembly.

The test stud assembly was cured at 150°C for 1 hour. After curing, the test stud assembly was allowed to cool to room temperature before testing. A photograph of the test stud assembly is shown in Figure 13.

The stud test assembly was then loaded onto the Seabastian tester for the film adhesion strength measurement. The stud was inserted into the platen on the tester and gripped tightly. The tester pulled the stud down against the platen supporting ridge until the film failed. The peak value was recorded from the display. The pulling rate was set at 9mm/sec. The tester and pulling test experiment are shown in Figure 14.

3.6 Oxidation test

3.6.1 Oxidation of the ZrB_2 thin film

The purpose of this experiment was to determine the oxidation kinetics of the ZrB_2 thin film at 1200°C in atmosphere. A gravimetric approach, in which the weight change with respect to time was recorded, was employed.

A wafer with ZrB_2 thin film coating on both sides was oxidized in a CM high temperature furnace. The film thickness was 1 μm . The wafer was heated up to 1200°C at 3.25 °C/min, held at 1200°C for 12 hours, and then cooled down to room temperature at 3.25 °C/min. After the wafer was cooled to room temperature, it was weighed with an Ainsworth analytic balance. The balance had an accuracy of 0.1 mg. The above procedures

A- test stud B- coated sample C- supporting plates

Fig.13 The test stud assembly

Fig.14 Adhesion test using Sebastian
Five multi-purpose tester

were repeated 16 times.

The accumulated weight change at each cycle was converted to the corresponding oxide thickness using Equation [17].

$$x = \Delta w / \pi r^2 \rho \quad [17]$$

where Δw is the weight change, r the radius of the sample, and ρ the density of the oxide.

A regression equation based on the experimental data was then obtained through statistical analysis. The results of this experiment yielded a plot of oxide thickness versus time

3.6.2 Pre-oxidation of ZrB₂ thin film

Because the oxide scale formed on the surface of ZrB₂ may function as an oxidation barrier, pre-oxidation of ZrB₂ film in a controlled manner has the possibility of increasing the oxidation resistance. For this reason, six wafers with 1 μm ZrB₂ films on both surfaces were pre-oxidized at 450°C, 600 °C and 900 °C. Two wafers were used at each temperature. The wafers were heated to the pre-oxidation temperatures at 1.5 °C/min, held at that temperature for 4 hours, and then cooled to room temperature at 1.5 °C/min. After pre-oxidation, one sample was examined by SEM for evidence of film damage introduced by pre-oxidation. The other was subjected to further oxidation.

3.6.3 Thermal cycling tests

In this experiment, one bare wafer, one as-sputtered wafer and three other wafers from the pre-oxidation experiment were subjected to oxidation under thermal cycling conditions. Their oxidation rates were compared with one another to determine which one had the best oxidation resistance. Table 6 summarizes the specimen characteristics used in this part of the study.

Table 6 Summary of specimen characteristics used in oxidation test

Specimen	Type of Sample	Sputtered Film Thickness (μm)	Pre-oxidation Status	Pre-oxidation Temperature
1	Bare wafer	0	No	N. A.
2	Sputtered wafer	1	No	N. A.
3	Pre-oxidized wafer	1	Yes	450 °C
4	Pre-oxidized wafer	1	Yes	600 °C
5	Pre-oxidized wafer	1	Yes	900 °C

The specimens were tested in the high temperature furnace. The cycle consisted of a 6-hr heat-up to 1200°C and 12-hr hold at 1200°C, followed by cooling to ambient temperature within 6 hours. The test was repeated for 16 cycles. For each cycle, the weight gain of the specimen,

resulting from the oxidation, was measured with the analytic balance after the specimens were cooled to ambient temperature. After 16 cycles, the specimens were examined under the scanning electron microscope. Failure of the specimen tested in this study was defined as delamination of the films or scales.

4. Results and Discussion

4.1 Deposition rates

Figure 15 shows the deposition rates of the ZrB_2 thin films at 280W r.f. input power, as a function of argon pressure. It can be seen from the figure that the deposition rate decreases when the argon pressure increases from 40×10^{-3} Torr to 75×10^{-3} Torr. This can be explained in terms of greater scattering of the sputtered species in the plasma, prior to arrival at the substrate, when the argon pressure is increased. The pressure dependence of the deposition rate, at constant r.f. power, is the combined result of ion current and back-scattering of sputtered atoms. It is known that the rate at which material is deposited at the substrate is proportional to the rate at which it is removed from the cathode, and may be represented by:

$$Q = CI\gamma \quad [17]^{(27)}$$

where Q is the deposition rate, C is a constant which characterizes the sputtering apparatus, I is the ion current, and γ is the sputtering yield. It would be apparent from Equation [17] that the maximum possible current should be used if the highest deposition rate is to be achieved. The only way to increase current without increasing power is to increase the pressure of the plasma. However, the pressure cannot be increased without limit, because increasing pressure leads to higher probability that sputtered atoms will return to the cathode by back-scattering, thus resulting in a deposition rate drop.

Fig. 15 Deposition rate as a function of argon pressure

It was also found that the plasma became unstable and even extinguished if the argon pressure was reduced below 40×10^{-3} Torr. This was due to the fact that as the argon pressure was reduced, the Crookes' dark space expanded towards the substrate. The current density begins to fall off very drastically when the cathode-anode spacing becomes comparable to the Crookes' dark space. This makes it difficult for self-sustaining of the glow discharge.

The influence of radio frequency power on the deposition rate of ZrB_2 thin films when argon pressure was held at 50×10^{-3} Torr is shown in Figure 16. As can be seen from the figure the deposition rate increases almost linearly with increasing r.f. power. This is due to the increasing ion current when rf power is increased. R.f. power levels greater than 1000 watts caused overheating of the cathode plate. This resulted in a rapid increase of reflected power. Thus, the rf power used for deposition was limited to 1000 watts.

Based on the above results, an optimal deposition condition was chosen in order to obtain a high deposition rate while maintaining a stable plasma. Table 7 lists these conditions as well as the deposition rate and substrate temperature under these conditions. It can be seen from Table 7 that the substrate temperature was low compared to the melting temperature of ZrB_2 . This indicated that the thermal energy of the species arriving at the substrate was low, and surface diffusion of the species along the substrate was very limited.

Fig. 16 Influence of r.f. power on deposition rate

Table 7 Summary of Optimal Deposition Condition

Argon Pressure	50×10^{-3} Torr
R.f. Power	800 Watts
Deposition Rate	103 Å/min
Substrate Temperature	250°C

4.2 Characteristics of the films

4.2.1 Scanning electron microscopy of the sputtered films

Scanning electron microscopy was performed to investigate the physical structure of the films. The SEM micrograph of the surface of an as-sputtered film is shown in Figure 17. The overall surface is featureless at a magnification of 2000 times, indicating a relatively smooth and dense film. No cracks were found. Some clusters and holes can be seen in the micrograph in Figure 17. The clusters are thought to be the nucleation spots formed on the initial dense films. The tendency to reduce surface energy leads to formation of spherical clusters. The formation of holes was due to the characteristics of nucleation and growth of films. The sputtered species first form small islands on the substrate. The islands then coalesce into a connected network structure and are flattened to increase surface coverage as sputtering proceeds. However, the network contains some empty spots. Filling of these empty spots is a slow process, which results in holes being left behind.⁽²⁸⁾

Figure 18 is a SEM micrograph of the cross section of the sputtered films, which were found to have a typical columnar structure. This columnar structure results from the difference in growth rates at the peaks and valleys of the surface topology, due to the shadowing effect.⁽²⁹⁾ Surface diffusion, as a competing mechanism, tends to smooth out the surface irregularities. The outcome of the competition between the inherent growth irregularities due to the shadowing and the stabilizing effects of

Fig. 17 SEM micrograph of as-sputtered film surface

Fig.18 Cross-section of as-sputtered film

surface diffusion determines the physical structure of the films. The substrate roughness serves as initial surface irregularities. If the length of the irregularities are less than the surface diffusion length, they can be smoothed out by surface diffusion. Therefore, whether or not columnar growth is expected depends on the length scale of the substrate surface roughness and the surface diffusion length, which is dictated by the deposition conditions. The structure zone model has proven very useful in providing an overview of the relationship between the microstructure of deposited films and the deposition parameters. The zone model is shown in Figure 19.⁽³⁰⁾ In this model, the microstructures of films are represented as a function of homologous temperature (T/T_m) by three zones, each with its own characteristic structure. The low temperature Zone 1 structure is columnar, consisting of tapered units. The Zone 2 structure consists of columnar grains, which are defined by metallurgical boundaries and increase in width with T/T_m in accordance with activation energies typical of surface diffusion.. The high temperature Zone 3 structure consists of equiaxed grains, which increase in accordance with activation energies typical of bulk diffusion.

Because of the high sputtering pressure (50 millitorrs) used in the experiment and low substrate temperature (250°C), the species arriving on the substrate had very low thermal energies. This resulted in very limited surface diffusion of the sputtered species along the substrate. Thus, the columnar structure of the sputtered films is reasonable. If the zone model is applied here, the microstructure of the sputtered films in the experiment fell into Zone 1. This gives a fine columnar structure.

Fig. 19 Zone model of sputtered films

4.2.2 Chemical composition of the as-sputtered films

The films were analyzed for Zr and Si qualitatively with a Kevex-3000 energy dispersive spectroscope. The results are shown in Figure 20. A very strong Zr peak appears on the spectrum, while the silicon peak is barely seen. This indicates that the silicon wafer was covered by the sputtered film. The thickness of the film was calculated as $9275 \text{ \AA}$, from multiplying the deposition rate by the deposition time.

The results of AES analysis is shown in Figure 21. The stoichiometry of the films was determined to be $\text{Zr:O} = 1.5 : 1$. Only a trace amount of boron was detected. The cause of this great deviation from the target stoichiometry is not understood at this time. It may have been caused by the following :

- The surface of the target had been oxidized. The oxide covered the target surface. Thus, the sputtering was not of the pure materials but of its oxides.
- The cathode temperature was too high, and B_2O_3 may, under this condition, have a significant vapor pressure which might lead to its evaporation from the cathode.
- Boron had a much higher sputter yield than Zr, thus the surface of the target was depleted of boron with continuous usage.

Fig. 20 Energy dispersive spectrum of as-sputtered film

Fig. 21 AES of as-sputtered films

- High argon pressure resulted in a very short mean free path. The very light boron atoms were scattered so many times by the much heavier argon atoms when they traveled from the target to the substrate only a few boron atoms made their way to the substrate.
- The low atomic number and electron energy of boron could make it relatively difficult for the detector to pick up boron's Auger electron signal during analysis of the specimen. Quantitative analysis using AES is based on counting Auger electron yield of the element. This yield is influenced to a great extent by the ability of the detector to detect the signal to be analyzed. Because the Auger electron energy of boron is low, Auger electrons from boron might lose their characteristic energy easily when traveling towards the detector. This could lead the detector to undercount the yield of the Auger electrons emitted by boron.

4.2.3 Adhesion strength of the sputtered films

The average adhesion strength of the sputtered films from the three tested specimens was found to be 545 kg/cm^2 . Good adhesion existed between the sputtered films and the silicon substrate. This suggests that some "interfacial phases" may exist between them. However, no study was carried out to investigate the formation of the "interfacial phases". Bonding may occur through the formation of intermediate oxides, such as SiO_2 and ZrO_2 , between the film and substrate. They would function as "adhesion-aiding" oxides. The native SiO_2 film on the silicon wafer may act as a

“bridge” here as the connection between the substrate and the sputtered film. The other factor that may contribute to this good adhesion is the refractoriness of ZrB_2 . Films of higher melting materials usually show better adhesion than those of lower melting materials because the lower melting materials have higher surface mobility, so that they agglomerate more easily. This would reduce the amount of contact surface between film and substrate and hence the total amount of adhesion.

4.3 Oxidation behavior of the sputtered films

Figure 22 shows the oxide thickness, x , of the sputtered films as a function of time, t , at 1200°C . The figure includes the experimental data and regression line based on those data. Only the density of ZrO_2 was used during calculation and the density of B_2O_3 was neglected, due to the fact that only trace amounts of boron were found in the film. The regression equation was found to be :

$$x = 0.24 t^{0.45} \quad [17]$$

The correlation coefficient of the regression equation [17] based on the experimental data is 0.998. It is apparent that the equation is very close to a parabolic relationship, which indicates that oxidation of the sputtered films was diffusion limited, and the oxide scale forming on the sputtered films was continuous and protective. The parabolic rate constant is 0.24. The SEM micrograph of the sample surface after 192 hours exposure at 1200°C , as shown in Figure 23, confirms this. It can be seen from Figure

Fig. 22 Oxidation kinetics of r.f. sputtered ZrB_2 films

Fig.23 SEM micrograph of sputtered films
after 192 hours exposure at 1200°C

23 that the surface became rough after exposure. However, no severe cracking and spalling appeared. The oxide scale was continuous and adherent. This continuous and adherent oxide scale contributed to the oxidation resistance of the sputtered films.

These results were much in line with the study reported by J.J. Funngon and R.A. Lux. They also reported that oxides on the surface of ZrB_2 film developed with a parabolic dependence on oxidation time. However, the report did not give a regression equation.

The deviation of the regression equation from a perfectly parabolic relationship may be due to the following factors:

1. The exposure was not isothermal. The periodic withdrawing of the sample from the furnace for weight change determination might have caused cracking, delamination and spalling of the films.
2. It was not possible to eliminate oxidation during the ramp-up and ramp-down periods.

4.4 Micrography of pre-oxidized specimens

Pre-oxidation of the sputtered films was done at 400°C , 600°C and 900°C . Figure 24, 25, and 26 are SEM micrographs of the pre-oxidized specimens at these temperatures. Noticeable oxide scales can only be observed on the specimen that was pre-oxidized at 900°C . Comparison of

Fig.24 SEM micrograph of sputtered films pre-oxidized at 400°C

Fig.25 SEM micrograph of sputtered films pre-oxidized at 600°C

Fig.26 SEM micrograph of sputtered films pre-oxidized at 900°C

these specimens with as-sputtered specimens reveals that pre-oxidation of the sputtered films caused cracking and spalling in some parts of the film. This was thought to be due to the thermal stresses imposed on the films during heating and cooling.

4.5 Results from cyclic oxidation exposure

The results of cyclic oxidation tests for both bare and coated silicon wafers, as well as specimens with pre-oxidized coatings, are plotted in Figure 27. The continuous curves are the regression curves based on the experimental data, and the error bars indicate $\pm 5\%$ error from the corresponding regression curves. Compared to the bare silicon wafer, the oxidation rates of the ZrB_2 coated wafers were reduced significantly. The reduction of the oxidation rates is thought to be due to the following:

1. The continuous sputtered films on the silicon surface protected the silicon from direct contact with air. Because of this, it was the sputtered films that were being oxidized rather than the silicon substrate.
2. As discussed earlier, the ZrO_2 scale formed on the sputtered films was protective. It functioned as an oxygen diffusion barrier. This oxide scale gave the sputtered films good oxidation resistance. In addition, ZrO_2 has low thermal conductivity. It reduced the heat flux to the inner layers so that the oxidation reaction occurring on the interface was retarded.

A- regression curve for bare wafer B- regression curve for coated wafer
 C- regression curve for coating pre-oxidized at 400°C
 D- regression curve for coating pre-oxidized at 600°C
 E- regression curve for coating pre-oxidized at 900°C

Fig. 27 Comparison of oxidation rates of bare silicon, ZrB₂-coated silicon, and silicon wafers with pre-oxidized ZrB₂ coatings

3. A ZrO_2 scale is more adherent and protective than a SiO_2 scale, as was predicted from the P-B ratios. This becomes obvious by comparing the SEM micrographs of the bare and coated specimens after oxidation testing. The micrographs are shown in Figures 28, 29 and 30. As can be seen from these micrographs, the oxide scale on the bare wafer became severely cracked and spalled after oxidation, while oxide scales on the coated wafers still remained adherent and continuous. Because of the spalling and cracking of the oxide scales of a bare silicon, diffusion of oxygen into the oxide layer became much easier and faster than into those with the coatings. The ease with which oxygen diffused into the oxide scales of bare silicon led to the high oxidation rate of bare silicon.

It can also be seen from Figure 27 that pre-oxidation of the sputtered films did not improve the oxidation resistance of the films. When the pre-oxidation temperature was 400°C , the oxidation rates remained almost the same as those of the sputtered films. As the pre-oxidation temperature increased to 600°C the oxidation rates increased, due to film spalling during the pre-oxidation period. This can be seen from Figure 24. At 900°C , oxidation rates dropped below those at 600°C . This can be explained by the fact that the pre-oxidized layer became thicker at 900°C than that at 600°C , because of the rapid increase of oxidation rate of ZrB_2 above 600°C . This thicker oxide layer increased the oxygen diffusion distance towards the substrate, and thus retarded the oxidation rates. The lowest oxidation rates at 900°C , among the three pre-oxidation temperatures, suggest that the

Fig. 28 SEM micrograph of bare silicon after
192 hours exposure at 1200°C

Fig. 29 SEM micrograph of ZrB₂-coated silicon
after 192 hours exposure at 1200°C

Fig. 30 SEM micrograph of silicon with pre-oxidized
ZrB₂ coating after 192 hours exposure at 1200°C

best pre- oxidation temperature be 900°C .

5. Conclusions

Overall, the objectives of the study were fulfilled. The experimental data showed that oxidation of ZrB_2 thin films followed the parabolic relationship. This indicated that oxidation of the thin films was diffusion limited. Examination of the samples after 190 hours exposure at 1200°C showed no severe cracking or spalling. This observation matched the expectation based on P-B ratios, and thus the oxide scales on the thin films were protective. Comparison of oxidation for coated and bare silicon wafers showed that applying ZrB_2 films on the silicon surface reduced the oxidation rate of silicon significantly. The oxidation resistance was due mainly to formation of protective oxide scales on the surface of ZrB_2 .

Due to the defects introduced during heating and cooling, preoxidation of the thin films did not improve the film's oxidation resistance as was expected. However, pre-oxidation at 900°C gave the best result among the three different temperatures investigated. In the future, if slower heating and cooling rates are utilized to avoid thermal stress induced damage to the films, preoxidation might be able to improve the oxidation resistance of the sputtered films.

R.f sputtering has proved to be a good and simple approach to deposit ZrB_2 films. The films exhibited the typical columnar structure under the operating conditions used in the sputtering process. As-sputtered films had excellent coverage and high adhesion on the silicon wafers. But stoichiometry of the sputtered films deviated significantly from that of the

target. The reason for this deviation is not understood and was not investigated due to lack of analytical facilities and time. This too would be a topic for future study.

6. References

1. Siegfried Mochizuki, Kimie Funahashi, and Kazuyuki Kurosawa, "ZrB₂ coated copper plate by chemical vapor deposition, and its corrosion and oxidation stability" Thin Solid Films , 189 (1990), p. 73.
2. I. M. Low, "Fabrication of new zirconium boride ceramics" J. Materials Science Letters , March, 1989, p. 1281.
- 3 W. C. Tripp, "Thermogravimetric study of the oxidation of ZrB₂ in the temperature of 800°C to 1500°C" J. Electrochem Society: Solid State Science, July 1971, p. 1197.
4. U. K. Chakrabarti, H. Borz, and W. C. Dautremont-Smith, "Deposition of zirconium boride thin films by direct current triode sputtering" J. Vac. Science and Technology, 5(3), March, 1987. p. 107.
5. J. R. Shappirio and J. J. Finnegan, "Synthesis and properties of some refractory transition metal diboride thin films" Thin Solid Films , 107 (1983), p. 81.
6. E. Randich, P. P. Aured, "Chemical vapor deposited ZrB₂ as a selective solar absorber" Thin Solid Films , 83 (1981), p. 394.
7. J. C. Scully, The Fundamentals of Corrosion, Pergamon Press, 1990, p. 18

8. William D. Callister, Materials Science and Engineering, An Introduction, John Wiley & Sons, Inc., 1991, p. 592.
9. William D. Callister, Materials Science and Engineering, An Introduction, John Wiley & Sons, Inc., 1991, p. 593.
10. S. F. Chang: "Zirconia packed aluminized Co-29Cr-6Al thermal barrier coatings" J. Vac. Sci. Technology A, 9(4) July/Aug., 1991, p. 2099.
11. Ram Kossowsky, Surface Modification Engineering Volume II p55
12. Graig R. Barrett, William D. Nix, Alan S. Tetelman, The Principles of Engineering Materials , Prentice-Hall Inc., 1973, p. 181.
13. Kingery, Bowen, Uhamann, Introduction to Ceramics, John Wiley & Sons Inc., 1976, p. 240.
14. Norman L. Peterson, Norman L. Peterson Memorial Symposium: oxidation of metals and associated mass transportation, Warrendale, Pa., 1986, p. 11.
15. William D. Callister, Materials Science and Engineering, John Wiley & Son, Inc., 1991, p. 594.

16. William D. Callister, Materials Science and Engineering, John Wiley & Son, Inc., 1991, p. 595.
17. J. J. Finnegan, R. A. Lux, "Resistivity, oxidation kinetics and diffusion barrier properties of thin film ZrB_2 " Thin Solid Films, 119, (1984) 23-30, p. 27.
18. E. Randich, P.P Aured, "Chemically vapor deposited ZrB_2 as a selective solar absorber" Thin Solid Films , 83(1981), p. 394.
19. J. J. Finnegan, R. A. Lux, "Resistivity, oxidation kinetics and diffusion barrier properties of thin film ZrB_2 " Thin Solid Films, 119, (1984) 23-30, p. 27 - p. 29.
20. George S. Brady, Materials Handbook , McGraw-Hill, 1962, p. 661.
21. Roy M. Adam, Boron, Metallo-Boron Compounds & Boranes, Interscience Publisher, 1964, p. 312.
22. G. V. Samsonov, Handbook of High Temperature Materials, Plenum Press, 1964, p. 354.
23. G. V. Samsonov, The Oxide Handbook, IFI/Plenum, 1982, p. 108.
24. Kingery, Bowen, Uhlmann, Introduction to Ceramics, John Wiley & Son, 1976, p. 68.

25. David R. Lide, Handbook of Chemistry and Physics, CRC Press, 1992, p. 5-66.
26. S. Wolf, R.N. Tauber, Silicon Processing For the VLSI Era (Volume 1), Lattice Press, 1986, p. 336.
27. Berry, Robert W, Thin Film Technology, Van Nostrand, 1968, p. 205.
28. Chopra, Kasturi, Thin Film Phenomena, Gcgraw-Hill, 1969, p. 165.
29. Joho A Thoronton, "The microstructure of sputtered-deposited coatings" J. Vac. Sci. Technology A4(6) Nov. 1986 p. 59.
30. B. A. Movchan, A. V. Pemchishin, "Zone model" Phys Met. Metallurgy 28(1969), p. 83.

7. Appendix

A. Data from oxidation test

Weight measurements from each oxidation cycle

	Wafer	Coated wafer	Coating pre-oxidized at 400°C	Coating pre-oxidized at 600°C	Coating pre-oxidized at 900°C
Stage	m (g)	m (g)	m (g)	m (g)	m (g)
0	0.3053	0.3042	0.3080	0.3046	0.3077
1	0.3074	0.3054	0.3094	0.3062	0.3086
2	0.3078	0.3058	0.3098	0.3077	0.3093
3	0.3082	0.3062	0.3103	0.3080	0.3099
4	0.3085	0.3065	0.3106	0.3081	0.3102
5	0.3087	0.3068	0.3109	0.3082	0.3105
6	0.3089	0.3070	0.3111	0.3084	0.3107
7	0.3091	0.3071	0.3113	0.3085	0.3109
8	0.3095	0.3073	0.3114	0.3086	0.3110
9	0.3099	0.3075	0.3115	0.3087	0.3112
10	0.3100	0.3076	0.3116	0.3089	0.3113
11	0.3103	0.3077	0.3118	0.3090	0.3114
12	0.3107	0.3080	0.3120	0.3090	0.3115
13	0.3109	0.3081	0.3122	0.3091	0.3117
14	0.3110	0.3081	0.3122	0.3092	0.3118
15	0.3112	0.3082	0.3123	0.3093	0.3119
16	0.3114	0.3083	0.3124	0.3094	0.3200

Accumulated weight change of the specimens during oxidation test

	Wafer	Coated wafer	Coating pre- oxidized at 400°C	Coating pre- oxidized at 600°C	Coating pre- oxidized at 900°C
Stage	Δm (g)	Δm (g)	Δm (g)	Δm (g)	Δm (g)
0	0	0	0	0	0
1	0.0021	0.0012	0.0014	0.0016	0.0009
2	0.0025	0.0016	0.0018	0.0031	0.0016
3	0.0029	0.0020	0.0023	0.0034	0.0022
4	0.0032	0.0023	0.0026	0.0035	0.0025
5	0.0034	0.0026	0.0029	0.0036	0.0028
6	0.0036	0.0028	0.0031	0.0038	0.0030
7	0.0038	0.0029	0.0033	0.0039	0.0032
8	0.0042	0.0031	0.0034	0.0040	0.0033
9	0.0046	0.0033	0.0035	0.0041	0.0035
10	0.0047	0.0034	0.0036	0.0043	0.0036
11	0.0050	0.0035	0.0038	0.0044	0.0037
12	0.0054	0.0038	0.0040	0.0044	0.0038
13	0.0056	0.0039	0.0042	0.0045	0.004
14	0.0057	0.0039	0.0042	0.0046	0.0041
15	0.0059	0.0040	0.0043	0.0047	0.0042
16	0.0031	0.0041	0.0044	0.0048	0.0043

Calculated results of oxide thickness

	Wafer	Coated wafer	Coating pre-oxidized at 400°C	Coating pre-oxidized at 600°C	Coating pre-oxidized at 900°C
Stage	Thickness (μm)	Thickness (μm)	Thickness (μm)	Thickness (μm)	Thickness (μm)
0	0	0	0	0	0
1	1.7078	0.7361	0.8523	0.9786	0.5524
2	2.0528	0.9786	1.0891	1.8783	0.9786
3	2.3647	1.2154	1.4048	2.0677	1.3416
4	2.6274	1.4048	1.5784	2.1308	1.5153
5	2.8026	1.5784	1.7678	2.194	1.7047
6	2.9778	1.7047	1.8783	2.3045	1.8309
7	3.1091	1.7678	2.0046	2.3676	1.9419
8	3.4592	1.8783	2.0677	2.4307	2.0046
9	3.766	2.0046	2.1309	2.4939	2.1308
10	3.8536	2.0677	2.194	2.6202	2.194
11	4.1163	2.1308	2.3045	2.6675	2.2413
12	4.4228	2.3045	2.4307	2.6675	2.3045
13	4.598	2.3676	2.557	2.7306	2.4307
14	4.6856	2.3676	2.557	2.7938	2.4939
15	4.8607	2.4307	2.6201	2.8569	2.557
16	5.0359	2.4936	2.6675	2.9201	2.6201

Note:

Density of SiO₂ is 2260kg/m³, and density of ZrO₂ is 6270kg/m³.

Regression equations of oxide thickness versus time for testing specimens

1. For wafer:

$$T = 1.54 \times t^{0.40} \quad R = 98\%$$

2. For coated wafer:

$$T = 0.74 \times t^{0.45} \quad R = 99\%$$

3. Coating pre-oxidized at 400°C:

$$T = 0.86 \times t^{0.42} \quad R = 99\%$$

4. Coating pre-oxidized at 600°C:

$$T = 1.28 \times t^{0.35} \quad R = 93\%$$

5. Coating pre-oxidized at 900°C:

$$T = 0.68 \times t^{0.51} \quad R = 98\%$$

where T=oxide thickness, t=exposure time, and R=correlation coefficient

B. Calculation of standard free energy of formation for ZrB_2 and ZrO_2

1. Standard free energy of formation for ZrB_2 :

Known: $\Delta H_{298}^{\circ} = -76700 \text{ cal/mole}$ $\Delta S_{298}^{\circ} = -1.8 \text{ cal/mole}$
 $\Delta C_p = 11.78 + 9.986 \times 10^{-3} T - 4.028 \times 10^{-6} T^2$

Because $\Delta G_T^{\circ} = \Delta H_{298}^{\circ} + \int_{298}^T \Delta C_p \cdot dT - T \Delta S_{298}^{\circ} - T \int_{298}^T (\Delta C_p / T) dT$

$$\int_{298}^T \Delta C_p \cdot dT = -3918.3 + 11.78T + 0.005T^2 - 1.3 \times 10^{-6} T^3$$

$$\int_{298}^T (\Delta C_p / T) dT = 11.78 \ln T - 9.986 \times 10^{-3} T - 2.0 \times 10^{-6} T^2 - 69.9$$

So $\Delta G_T^{\circ} = -80618.3 + 83.48T + 0.015 T^2 + 7 \times 10^{-7} T^3 - 11.78T \ln T$

T (K)	ΔG_T° (cal/mole)
298	-74389.98
300	-74362.57
400	-73013.28
500	-71644.84
600	-70192.59
700	-68612.41
800	-66871.68
900	-64944.98
1000	-62811.62
1100	-60454.32

(Data for ΔH_{298}° , ΔS_{298}° , and ΔC_p taken from Properties Index by G. V. Samsonov)

2. Standard free energy of formation for ZrO_2

$$\Delta G_T^\circ = -(259940 + 4.33T \log T - 59.12T) \text{ (calmole)}$$

T (K)	ΔG_T° (calmole)
298	-245514.82
300	-245421.78
400	-240798.77
500	-236223.27
600	-231685.64
700	-227179.49
800	-222700.30
900	-218244.68
1000	-2213810.00
1100	-209394.15

3. Standard free energy of formation for B_2O_3

$$298\text{K} - 700\text{K} \quad \Delta G_T^\circ = -304456.7 + 16.1T \text{ (calmole)}$$

$$700\text{K} - 2000\text{K} \quad \Delta G_T^\circ = -300182.8 + 58.3T \text{ (calmole)}$$

T (K)	ΔG_T° (calmole)
298	-299658.9
300	-299626.7
400	-298016.7
500	-296406.7
600	-294796.7
700	-293186.7
800	-253542.8
900	-247712.8
1000	-241882.8
1100	-236052.8

(Data for ΔG_T° taken from Handbook of Chemistry and Physics by David R. Lide)

C. Result from adhesion test

Specimen	Adhesion strength (kg/cm ²)
1	547
2	542
3	546
Ave.	545

D. Calculation of P-B ratio for ZrB_2

1. P-B ratio for ZrO_2 on ZrB_2 :

$$\begin{aligned}\text{P-B ratio} &= (A_{\text{ZrO}_2} \times \rho_{\text{ZrB}_2}) / (A_{\text{ZrB}_2} \times \rho_{\text{ZrO}_2}) \\ &= (123 \times 6.02) / (113 \times 6.27) \\ &= 1.05\end{aligned}$$

1. P-B ratio for B_2O_3 on ZrB_2 :

$$\begin{aligned}\text{P-B ratio} &= (A_{\text{B}_2\text{O}_3} \times \rho_{\text{ZrB}_2}) / (A_{\text{ZrB}_2} \times \rho_{\text{B}_2\text{O}_3}) \\ &= (70 \times 6.02) / (113 \times 1.84) \\ &= 2.02\end{aligned}$$

where A represents formula weight, and ρ density.