

(45)

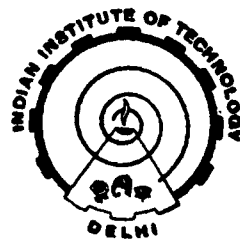
STRUCTURE AND MECHANICAL PROPERTIES OF R. F. REACTIVE MAGNETRON SPUTTERED TUNGSTEN CARBIDE FILMS

By

P. K. SRIVASTAVA

CENTRE FOR MATERIALS SCIENCE AND TECHNOLOGY

Thesis submitted
in fulfillment of the requirements
of the degree of
DOCTOR OF PHILOSOPHY



to the

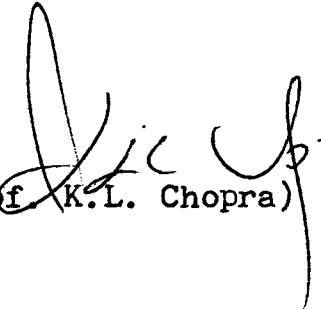
INDIAN INSTITUTE OF TECHNOLOGY, DELHI


December, 1985

TO MY PARENTS

CERTIFICATE

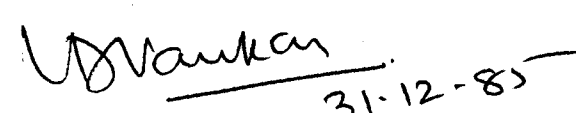
I am satisfied that the Thesis presented by P.K. Srivastava is worthy of consideration for the award of the Degree of Doctor of Philosophy and is a record of the original bonafide research work carried out by him under my guidance and supervision and that the results contained in it have not been submitted in part or full to any other university or institute for award of any degree/diploma.


(Prof. K.L. Chopra) 21/12/85


(Dr. V.D. Vankar) 31.12.85

THESIS SUPERVISORS:


PROFESSOR R.L. CHOPRA
HEAD, THIN FILM-SOLID STATE TECHNOLOGY LABORATORY
DEPARTMENT OF PHYSICS
INDIAN INSTITUTE OF TECHNOLOGY
NEW DELHI-110016, INDIA


DR. V.D. VANKAR
ASSISTANT PROFESSOR
CENTRE FOR MATERIAL SCIENCE & TECHNOLOGY
INDIAN INSTITUTE OF TECHNOLOGY
NEW DELHI-110016, INDIA

ACKNOWLEDGEMENT

I am deeply grateful to Professor K.L. Chopra and Dr. V.D. Vankar for their invaluable guidance, continuous encouragement, objective criticism and inspiration during all stages of this work. I consider it as a great privilege to have worked under them, who introduced me into this field and offered excellent facilities to carry out research work.

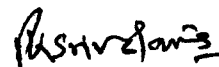
I am also grateful to Dr. S.C. Kashyap for the help rendered by him during the course of investigation.

It is a pleasure to acknowledge the help and cooperation extended by all the members of Thin Film Laboratory. Thanks are due to my colleagues A.N. Tiwari, Vandana Agrawal, Satyendra Kumar, Ajay Agrawal and R.S. Rastogi for their helping hand and useful discussions. I also wish to thank my friends, Anil Kumar, S.K. Khare, Sunil Saxena, R.A. Ray, N.P. Singh and Rishi Srivastava, for their help.

All the help rendered by M. Bhatnagar, Dr. K.C. Nagpal and Mr. Duggal during the course of investigation is gratefully acknowledged.

Special thanks to Mr. V.N. Sharma and Mr. N.S. Gupta for skilful preparation of this Thesis.

Above all, I am deeply indebted to my family members for their encouragement throughout my research work.



(P.K. SRIVASTAVA)

ABSTRACT

In the present work tungsten carbide films have been prepared by r.f. reactive magnetron sputtering on stainless steel substrates held in temperature range 200-500°C. Two different geometrical modes, normal mode and high rate mode, have been used to deposit various films. The effect of various parameters, like sputtering pressure, gas flow, substrate temperature, self bias developed on the cathode and the power applied have been optimized to obtain a hard, adherent film. Uniformly distributed fine grains (~ 200 to 400 \AA) of tungsten carbide films with columnar structure having regularly spaced columns ($\sim 300 \text{ \AA}$) have been obtained in these films. The films deposited in normal mode at lower substrate temperature ($T_s = 200^\circ\text{C}$) have a mixture of phases (f.c.c. B1 WC, hexagonal W_2C and A-15 W_3C) while the films deposited at higher substrate temperature (~ 300 to 500°C) have a single phase (f.c.c. B1 WC). On the other hand films deposited in high rate mode show a mixture of phases (hexagonal WC, A-15 W_3C , graphite and diamond carbon) at all temperatures (300 to 500°C). The amount of diamond phase in the films deposited at higher temperature ($\sim 500^\circ\text{C}$) is found to be more than in the films deposited at lower temperature, whereas the amount of graphite phase is less in films deposited at higher temperature as compared to that in low temperature deposited film. AES study of these films suggests that these films are nonstoichiometric and have same composition throughout the thickness. AES sputter depth

profile of thick films shows a very wide interfacial region due to intermixing of various species during sputtering process.

Microhardness, adhesion, friction and wear properties of these films have been reported. It is observed that the films prepared in the normal mode of deposition have very high microhardness value $\sim 3200 \text{ Kgf/mm}^2$, whereas the films prepared in high rate mode have microhardness $\sim 2365 \text{ Kgf/mm}^2$. The bulk hardness value of tungsten carbide is $\sim 1800 \text{ Kgf/mm}^2$. Under indentation load the films crack and a sequence of crack propagation with increasing load has been observed. The nature of crack propagation suggests that the films deposited in high rate mode at $T_s = 500^\circ\text{C}$ are more brittle than the films deposited in normal mode at $T_s = 500^\circ\text{C}$. Adhesion of the films has been measured by crack indentation method and a value $\sim 3.5 \times 10^7 \text{ grams/cm}^2$ has been observed in tungsten carbide films ($\sim 5.6 \mu\text{m}$ thick) deposited in normal mode.

Friction and wear of these films have been measured by pin and disc machine. It is found that the films deposited at 500°C in normal and in high rate mode have small coefficient of friction ~ 0.13 and 0.09 , respectively. The wear rates of tungsten carbide films deposited at $T_s = 500^\circ\text{C}$ in normal and high rate mode deposited on stainless steel are observed to reduce by a factor 20 as compared to bare substrates.

Thin layers ($\sim 1000 \text{ \AA}$) of titanium, tantalum, tungsten, silicon and molybdenum have been deposited on stainless steel substrate by r.f. diode sputtering. A mixture of phases (TiC (cubic) and TiO (cubic)) has been observed in titanium films, whereas a single face b.c.c. structure of tantalum, tungsten and molybdenum films have been observed. Silicon films are found to be amorphous. Thin layers ($\sim 1000 \text{ \AA}$) of tungsten carbide films have been deposited in normal mode on coated stainless steel substrate. AES depth profiling of these interlayer films show a wide intermixing ($\sim 1500 \text{ \AA}$) at the interface due to knock in effects. Complete mixing in the case of tantalum, tungsten, molybdenum interlayers has been observed. ESCA study suggests that the interlayer films are transformed in their respective carbides and no alloy formation between tungsten carbide/interlayer element/stainless steel has occurred.

Microhardness, adhesion, friction coefficient and wear resistance of the tungsten carbide films deposited on interlayer coated stainless steel substrate have also been reported. An improvement in wear life ~ 5 is observed in tungsten carbide-interlayer coated stainless steel substrates.

CONTENTS

	Page
ACKNOWLEDGEMENTS	
ABSTRACT	
CHAPTER I REFRACTORY METAL CARBIDE COATINGS	
1.1 Introduction	1
1.2 Application of Refractory Metal Compounds ..	3
1.3 Preparation of Refractory Metal Compounds ..	5
1.4 Composite Coatings of Refractory Metal Compounds	10
1.5 Tungsten Carbide Films	13
1.6 Present Work	16
CHAPTER II SPUTTERING PROCESSES	
2.1 Introduction	19
2.2 Sputtering Phenomenon	19
2.3 Magnetron Sputtering	23
2.4 Planar Magnetron Sputtering	26
2.5 Reactive Sputtering	28
2.6 Reactive Magnetron Sputtering	30
CHAPTER III EXPERIMENTAL DETAILS	
3.1 Introduction	33
3.2 Sputtering System	33
3.3 Cleaning and Polishing of Substrates	36
3.4 Deposition of Films	37
3.5 Film Thickness and Roughness Measurements ..	39

3.6	X-Ray Diffraction	41
3.7	Scanning Electron Microscopy	42
3.8	Auger Electron Spectroscopy	42
3.9	X-Ray Photoelectron Spectroscopy	43
3.10	Microhardness Measurements	44
3.11	Adhesion Evaluation	45
3.12	Friction and Wear Measurements	47
CHAPTER IV	STRUCTURE OF TUNGSTEN CARBIDE COATINGS		
4.1	Introduction	50
4.2	Results and Discussions	50
4.3	Conclusions	62
CHAPTER V	MICROHARDNESS, ADHESION, FRICTION AND WEAR PROPERTIES OF TUNGSTEN CARBIDE COATINGS		
5.1	Introduction	64
5.2	Results and Discussions	64
5.3	Conclusions	77
CHAPTER VI	STRUCTURE AND MECHANICAL PROPERTIES OF TUNGSTEN CARBIDE COATINGS ON SURFACE MODIFIED STAINLESS STEEL		
6.1	Introduction	78
6.2	Results and Discussions	79
6.3	Conclusions	92
CHAPTER VII	CONCLUSIONS AND SCOPE OF FURTHER WORK	93
APPENDIX I	Introduction	99
	Results and Discussions	99
REFERENCES		105
LIST OF PUBLICATIONS		123
BIO-DATA		124