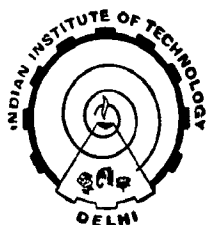


**INORGANIC THIN FILM MATERIALS  
FOR  
MICROLITHOGRAPHY**

by  
**PRAMOD KUMAR GUPTA**  
**Department of Physics**

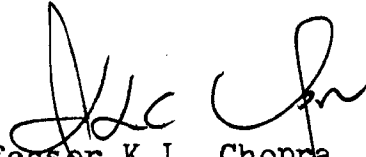
Thesis submitted  
in fulfilment of the requirements  
of the degree of  
**DOCTOR OF PHILOSOPHY**



**to the**  
**INDIAN INSTITUTE OF TECHNOLOGY, DELHI**  
**April, 1986**

CERTIFICATE

I am satisfied that the Thesis presented by Pramod Kumar Gupta 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.



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*Pramod Kumar Gupta*

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## ABSTRACT

In the present work, thin films of the following materials have been explored as inorganic resists: (i)  $WO_3$  as photo, electron and ion resist; (ii) obliquely deposited amorphous  $P_4Se_{10}$  as photoresist and  $Ag/P_4Se_{10}$  as photo and ion resist; (iii) amorphous Si as ion resist; (iv) amorphous  $MoO_3$  as ion resist; and (v) obliquely deposited amorphous  $Bi_{10}Ge_{20}Se_{70}$  as photoresist, and  $Bi_{10}Ge_{20}S_{70}$  and  $Ag/Bi_{10}Ge_{20}Se_{70}$  as photo and ion resist.

Thin films of amorphous and polycrystalline  $WO_3$  used in these studies were prepared by thermal and e-beam evaporation techniques. These films were found to change their colour on irradiation to UV light, e-beam and glow discharge hydrogen plasma and the coloured films showed insolubility in alkaline solution. The effect of colouration on the change in solubility has been studied by measuring the solubilities of electrolytically coloured and bleached films. This change in solubility on irradiation has been exploited for lithographic application. The effects of substrate temperature (during deposition and  $H_2$  plasma exposure) and the exposure time on etching rate and selectivity ratio have been studied. The lithographic parameters, sensitivity (S) and contrast ( $\gamma$ ), have been estimated. The contrast ( $\gamma$ ) values for a- $WO_3$  films exposed to photons, electrons and  $H_2$  plasma are  $\sim 2.3$ , 4, and 2.3, respectively, and for poly- $WO_3$  exposed to  $H_2$  plasma is  $\sim 3.3$ . The sensitivity (S) values for photons and electrons are  $\sim 10^{20}$  photons/cm<sup>2</sup> and  $\sim 10^{-3}$  C/cm<sup>2</sup>, respectively. Various patterns on these films

have been replicated by exposing the films to photons, electrons and H<sub>2</sub> plasma through a mask and by subsequent development in alkaline solution. In addition to these studies, the optical and electrical properties of the as-deposited and coloured films have been correlated with their etching characteristics.

Thin films of a-Si deposited by Kaufman ion-beam source and magnetron sputtering have been explored as ion and ion-beam resist materials. It has been observed that the etching rate of the exposed region in CF<sub>4</sub> plasma decreases compared to the unexposed region, thus giving rise to the negative tone behaviour. The effects of exposure time, substrate temperature (during plasma exposure), and H<sub>2</sub> (incorporated during deposition) concentration in the films on etching rate and selectivity ratio have been studied in detail. The sensitivity and contrast were found to be  $\sim 10^{18}$  ions/cm<sup>2</sup> and 1.1, respectively. A grating pattern of 20  $\mu\text{m}$  pitch by lift off technique and various other patterns have been replicated using this material as ion resist. The possibility of mask fabrication for deep UV lithography has been explored using a-Si as masking material. In addition to these studies, the effect of plasma exposure on etching characteristic of n-type single crystal Si has been studied and different patterns have been replicated.

Thin films of amorphous phosphorous decaselenide (P<sub>4</sub>Se<sub>10</sub>) deposited at an angle of 80° have been explored as photoresists. Depending upon the substrate temperature during plasma etching in CF<sub>4</sub> gas, both positive and negative tone behaviour of the photoresist have been observed. The effects

of substrate temperature, exposure time, and angle of deposition on etching rate and selectivity ratio have been studied. To estimate the lithographic parameters, the photon exposure characteristics of this material as positive and negative photoresists have been investigated. Contrast values of 2.5 and 2.9 for positive and negative, respectively, have been obtained with a sensitivity of  $10^{20}$  photons/cm<sup>2</sup> for both the photoresists. In addition to these studies on pure P<sub>4</sub>Se<sub>10</sub>, the thin films of Ag/P<sub>4</sub>Se<sub>10</sub> have been explored as photo and ion resist. The etching characteristics of this bilayer as photo and ion resist have been studied as a function of exposure time. The etching rates of this material have been found to decrease after photons and ions exposure, thus giving rise to negative tone of the resist. The contrast values of 2.9 and 5 for photon and ion irradiation, respectively, have been obtained.

Thin films of amorphous MoO<sub>3</sub> prepared by thermal evaporation have been explored as ion resists. It has been observed that when the films of MoO<sub>3</sub> are irradiated with hydrogen ions, these change their colour from light blue to dark blue and the solubility in alkaline solution decreases drastically. This change in solubility on colouration has been exploited for lithographic applications. The effects of substrate temperature (during plasma exposure) and exposure time on etching rate and selectivity ratio have been studied. The contrast value of 4.2 has been obtained. The optical properties of as-deposited and plasma coloured films and their correlation with etching characteristics have been studied.

Obliquely deposited thin films of amorphous  $\text{Bi}_{10}\text{Ge}_{20}\text{Se}_{70}$  ( $80^\circ$ ) as photoresists and  $\text{Ag}/\text{Bi}_{10}\text{Ge}_{20}\text{Se}_{70}$  ( $80^\circ$ ) and  $\text{Bi}_{10}\text{Ge}_{20}\text{S}_{70}$  ( $80^\circ$ ) as photo and ion resists have been explored for lithographic applications. Thin films without Ag overlayer showed a positive tone behaviour whereas a negative tone is observed with Ag overlayer. The effects of exposure time and angle of deposition on etching rate and selectivity ratio have been studied. The contrast values were found to vary from 1.25 to 5.0 depending upon the type of resist and the exposure tool used.

# CONTENTS

			Page
ACKNOWLEDGEMENTS			
ABSTRACT			
CHAPTER I	INTRODUCTION	.. ..	1
	1.1 Microlithography	.. ..	3
	1.1.1 The Lithographic Process	.. ..	5
	1.1.2 UV Lithography	.. ..	12
	1.1.3 E-Beam Lithography	.. ..	18
	1.1.4 X-ray Lithography	.. ..	24
	1.1.5 Ion Lithography	.. ..	30
	1.2 Etching	.. ..	36
	1.2.1 Pattern Transfer	.. ..	36
	1.2.2 Wet Chemical Etching	.. ..	41
	1.2.3 Dry Etching	.. ..	44
	1.3 Resist Systems	.. ..	61
	1.3.1 Resist Processes	.. ..	68
	1.3.2 Multilevel Resists	.. ..	78
	1.3.3 Inorganic Resists	.. ..	81
	1.4 Thesis Plan	.. ..	85
CHAPTER II	EXPERIMENTAL DETAILS	.. ..	87
	2.1 Preparation of Thin Films	.. ..	87
	2.1.1 Chalcogenide Based Materials	.. ..	87
	2.1.2 $WO_3$ and $MoO_3$	.. ..	88
	2.1.3 Amorphous Silicon	.. ..	90
	2.2 Thickness Measurements	.. ..	90
	2.3 Transmission Electron Microscopy	.. ..	91
	2.4 Optical Measurements	.. ..	91

	Page
2.5 D.C. Conductivity Measurements .. ..	92
2.6 Electrolytic Colouration and Bleaching	
Processes of WO <sub>3</sub> Films .. ..	92
2.7 Exposure Sources Used for Lithography ..	92
2.7.1 UV Light Exposure System .. ..	94
2.7.2 E-Beam Exposure System .. ..	94
2.7.3 Ion-Beam Exposure System .. ..	95
2.7.4 Glow Discharge Hydrogen	
Plasma Exposure System .. ..	96
2.8 Etching Characteristics Studies .. ..	98
2.8.1 Wet Chemical Process .. ..	98
2.8.2 Plasma Etching .. ..	98
2.9 Scanning Electron Microscopy .. ..	99
 CHAPTER III	
LITHOGRAPHIC PROPERTIES OF THE PHOTON, ELECTRON AND HYDROGEN PLASMA EXPOSED WO <sub>3</sub> FILMS .. ..	100
3.1 Introduction .. ..	100
3.2 Experimental Results .. ..	102
3.3 Discussion .. ..	116
3.4 Conclusions .. ..	125
 CHAPTER IV	
PLASMA PROCESSED p-Se AND Ag/p-Se FILMS AS RESIST MATERIALS .. ..	127
4.1 Introduction .. ..	127
4.2 Experimental Results .. ..	129
4.3 Discussion .. ..	143
4.4 Conclusions .. ..	148

CHAPTER V	AMORPHOUS AND CRYSTALLINE SILICON	
	AS ION RESIST MATERIALS	.. .. 150
	5.1 Introduction	.. .. 150
	5.2 Experimental Results	.. .. 154
	5.3 Discussion	.. .. 172
	5.4 Conclusions	.. .. 177
CHAPTER VI	LITHOGRAPHIC PROPERTIES OF HYDROGEN	
	PLASMA EXPOSED MoO <sub>3</sub> FILMS	.. .. 180
	6.1 Introduction	.. .. 180
	6.2 Experimental Results	.. .. 182
	6.3 Discussion	.. .. 185
	6.4 Conclusions	.. .. 193
CHAPTER VII	PLASMA PROCESSED Bi-Ge-X (X = Se, S) AND	
	Ag/Bi-Ge-Se FILMS AS RESIST MATERIALS	.. .. 195
	7.1 Introduction	.. .. 195
	7.2 Experimental Results	.. .. 197
	7.3 Discussion	.. .. 214
	7.4 Conclusions	.. .. 218
CHAPTER VIII	CONCLUSIONS AND SCOPE OF FURTHER WORK	.. .. 219
REFERENCES		.. .. 223
APPENDIX		
LIST OF PUBLICATIONS		