# SYNTHESIS, MICROSTRUCTURE AND MECHANICAL PROPERTIES OF CHROMIUM CARBIDE AND CHROMIUM NITRIDE FILMS

by

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TO MY PARENTS

# CERTIFICATE

I am satisfied that the Thesis entitled "Synthesis, Microstructure and Mechanical Properties of Chromium Carbide and Chromium Nitride Films" presented by Vandna Agarwal 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 her 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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## ABSTRACT

This thesis presents a detailed study of composition, structure and mechanical properties of reactively magnetron sputtered chromium carbide coatings and activated reactive deposited chromium nitride coatings. For chromium carbide films the substrate temperature and acetylene flow rate have been recognized as the important deposition parameters and effects of these on the composition, crystallographic structure and microstructure have been investigated. The carbon to chromium ratio in the film increases from $\sim$ 0.10 to $\sim$ 0.40 (at $T_s$ = 500°C) with increase in ratio of acetylene to argon flow rates (R) from 0 to 0.50. On increasing the substrate temperature from 30 to 500°C (at R = 0.5), C/Cr ratio increases from $\sim$ 0.26 to $\sim$ 0.40. AES and ESCA results reveal that carbon in the film is present as free carbon and in carbide form. A systematic variation of phases from a supersaturated solid solution of carbon and chromium to a mixture of chromium and $Cr_{23}C_6$ and subsequently to $Cr_{23}C_6$ is obtained with increasing acetylene flow rate. The crystallite size of the films having supersaturated solid solutio of carbon and chromium is lower than that of the $Cr_{23}C_6$ films. Hydrogen and hydrocarbon radicals (CH, $CH_2$, $C_2H$, $C_2H_2$ etc.) are incorporated in the films and the amount of incorporated hydrogen and hydrocarbon radicals decreases with increasing R. The films having a supersaturated solid solution of carbon and chromium exhibit a fine grained, smooth and dense structure. However, the hydrogen incorporation in the films results in a rough and porous microstructure. Whereas at higher acetylene flow rate,

the incorporated carbon in the film reduces the roughness and porosity.

Mechanical properties such as microhardness, adhesion, friction coefficient and wear of these films depend on the composition and microstructure of these films. The variation of mechanical properties with acetylene flow rate and film thickness has been studied. Best mechanical properties are obtained for the films having a solid solution of carbon and chromium (R = 0). Fine grain size, smooth and dense microstructure and incorporation of carbon in chromium matrix lead to high values of microhardness $\sim$5000 Kgf/mm$^2$ and adhesion $\sim 4.4 \times 10^7$ gms/cm$^2$, and low value of friction coefficient $\sim$ 0.11 and wear ($R_{CLA}$ = 0.10 $\mu$m). With increase in R to 0.25 a decrease in microhardness and adhesion values, and an increase in friction coefficient and wear have been observed due to large grain size, rough and porous microstructure alongwith the carbide formation. Further increase in R to 0.50 results in an improvement of mechanical properties.

Annealing of these films results in an increase in grain size and modification of surface texture. However, no change in the composition of the films is observed on annealing. On annealing, films having a supersaturated solid solution of carbon and chromium transform to a mixture of chromium, $Cr_{23}C_6$ and $Cr_3C_2$ phases and consequently a drastic decrease in microhardness value is observed. Films having a mixture of chromium and $Cr_{23}C_6$ phase show the presence of $Cr_7C_3$ and $Cr_3C_2$ phases alongwith $Cr_{23}C_6$ after annealing and an increase in microhardness is observ due to reduced porosity. However, $Cr_{23}C_6$ films, when annealed

exhibit $Cr_7C_3$, $Cr_3C_2$ and $Cr_{23}C_6$ phases and a slight decrease in microhardness values is observed.

Chromium nitride films are synthesized by evaporation of chromium in an ammonia plasma at $\sim 1x10^{-2}$ Torr. As the substrate temperature increases from 30 to 500°C, the nitrogen concentration in the films increases from 0.02 to 0.85 and a variation from solid solution of nitrogen and chromium to $Cr_2N$ and subsequently to CrN phase have been observed. Hydrogen and hydrogen containing species like NH and $NH_2$ have been observed at the surface of these films but in the bulk of the film only hydrogen has been observed. Amount of hydrogen decreases with increase in substrate temperature.

Electron beam evaporation of chromium in an ammonia plasma at $\sim 1x10^{-4}$ Torr results in the formation of A-15 phase under certain deposition conditions. This phase is metastable phase which transforms to A-2 phase of chromium at $\sim$ 500°C. At lower substrate temperatures, a mixture of both phases is observed. With increase in deposition rate to $\sim$ 4500 Å/min., formation of A-2 phase takes place. SIMS studies suggest that A-15 phase of chromium may be stabilized by the presence of H, NH and $NH_2$ species in the film.

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