7.1 Over all summary

This thesis encompasses with the principal objective to deposit DLC films over AISI SS304 substrates with a) reduced internal stress b) improved adhesion c) low coefficient of friction and d) better hardness by using different film architecture. Earlier work done by other authors on DLC films on addressing these problems used hybrid deposition techniques and complicated film architectures such as gradient multilayers with multiple dopants and adopted complicated methodology in order to obtain better mechanical and tribological property of DLC film with good adhesion. The proposed methods were economically costly, tedious and time consuming. Therefore, the present work has employed simple film architectures such as nanocomposite, bilayer and multilayer films by using transition metals as dopant and interlayer in order to enhance the mechanical and tribological property of the film and also the adhesion strength by reducing the internal stress of the film.

In order to achieve the objective of the work the first aim was targeted towards the deposition of DLC film on AISI SS304 substrate by PLD technique. Since, the mechanical and tribological properties are controlled by the sp\(^3\) fraction of the DLC film which in turn was controlled by the PLD deposition parameters. Therefore, the PLD parameters such as laser power density, substrate temperature, target to substrate distance, laser repetition rate were optimized in order to obtain DLC film with high sp\(^3\) fraction. Visible and UV Raman spectroscopy was used as the main tool to evaluate the microstructure of the DLC films and also to qualitatively obtain the sp\(^3\) fraction in the
film by using Ferrari three stage model [115]. EELS and XPS were used to measure the
sp³ content quantitatively. The DLC film with maximum 68 % of sp³ content was
achieved with the optimized PLD parameters. The monolithic DLC films though
exhibited low friction coefficient and high sp³ fraction but due to internal compressive
stress, the films spall off from the substrate. Therefore, the addition of transition metals
as dopant or interlayer was necessary in order to improve the adhesion strength of the
film.

The second aim of the work was targeted towards investigating the mechanical and
tribological properties of DLC/TM (TM = Ag, Cr, Ti & Ni) nanocomposite films
deposited on to AISI SS304 substrate by PLD technique. The metal dopants were varied
through 5 to 20 at % in the DLC matrix. Significant reduction of internal stress as high as
6 GPa was observed for DLC films with low metal concentration. The addition of the
metal dopant resulted in the shift in G peak towards lower wavenumber indicating
decrease of the internal compressive stress of the DLC film. The formation of TiC and
CrC phases in DLC/Ti and DLC/Cr nanocomposite films respectively, were confirmed
from XPS and GI-XRD studies which enhanced the hardness and adhesion of the film
compared to monolithic DLC film. The metals doped in the DLC film formed
nanoclusters in the DLC matrix as confirmed from the HRTEM studies. The adhesion
strength of the film was improved by adding metal dopants and better adhesion was
obtained for DLC films with high metal concentration. The hardness of the DLC film
reduced on addition of metal dopant in the film. No particular trend was observed for the
friction behavior of the DLC films with different metal concentration. Though,
unanimously unstable and oscillatory friction behavior was observed for DLC film with
high metal concentration for the case of carbide formers (Ti & Cr). DLC/TM nanocomposite film with 5-15 at % metal dopant exhibited low friction coefficient. The introduction of metal as dopant in DLC film though enhanced the adhesion strength of the film when compared to monolithic DLC film but the hardness of the film was found to decrease with the addition of the metal in the DLC film.

Therefore, the third aim of the work was to introduce TM as interlayer between DLC and substrate and to study the mechanical and tribological property DLC/TM (TM = Ag, Cr, Ti & Ni) bilayer films deposited by PLD technique on to AISI SS304 substrate. The thickness of the transition metal interlayer was optimized in order to obtain better adhesion of the film to the substrate. The interlayer thickness was optimized to ~ 30 nm which resulted in better adhesion of the film. The SIMS profile of DLC/Ti and DLC/Cr showed mixing of phases at the metal carbon interface. This confirms the formation of TiC and CrC at the interface which resulted in the high hardness of the DLC/Ti and DLC/Cr bilayer films with hardness value of 15 and 12 GPa respectively. The introduction of metal interlayer between DLC and steel substrate resulted in enhanced hardness of the film compared to the monolithic DLC film. Low friction coefficient of DLC/TM bilayer films was obtained in the range 0.2 -1. DLC/TM bilayer films exhibited good mechanical and tribological property but the adhesion of the film was low.

The fourth aim of the work was to introduce transition metals as thin layers to form the multilayer structure and to study the mechanical and tribological property of DLC/TM (TM = Ag, Cr, Ti & Ni) multilayer films deposited by PLD technique on to AISI SS304 substrate. The chemical behavior of DLC film remains similar with all the transition metal interlayer. However, interfacial adhesion measured by scratch test is significantly
enhanced in DLC/Ni and DLC/Ti interlayer systems due to formation of energetically favorable and defect free interface. The adhesion strength was measured to be 150 N for the DLC/Ni multilayer film which was reported for the first time using simple architecture and using nanosecond PLD technique. Hardness of these interlayer systems is also found to be higher compared to DLC/Cr and DLC/Ag films. Scratch resistance and graphitized tribofilm in DLC/Ni and DLC/Ti systems are found to be the main reason for low values of friction coefficient and high wear resistance. Low friction coefficient exhibited by DLC/Ni multilayer system is attributed to formation of carbonaceous transfer layer and absence of metallic oxide on the ball counterface during sliding. In addition, superior interface stability of the film is a contributing factor towards reduced wear. Therefore it can be concluded that DLC/TM multilayer films deposited by PLD technique exhibited better hardness, low friction coefficient and high adhesion strength compared to DLC/TM bilayer and nanocomposite films.

### 7.2 Future scope

In the present work DLC/Ni multilayer film exhibited very high adhesion strength of 150 N. Characterization techniques like SIMS, Raman spectroscopy and FE-SEM has revealed the chemical changes, phase transformation and alignment of metallic element at the carbon metal interface. To support these experimental results the future work can be extended to frame a theoretical simulation model to explain the atom by atom bonding that takes place at C and Ni interface which resulted in good adhesion of the film.