PLASMA DEPOSITED DIAMOND-LIKE FILMS FOR IR DEVICE APPLICATIONS

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Diamond-like carbon films synthesized by plasma processes have been investigated for their applicability to infrared optical devices. The films have been characterized for their physico-chemical properties. Optical device development with evaporation, sputtering and a novel hybrid process yielded efficient and durable devices in the IR band. Studies revealed the optically active and neutral roles of DLC films. Hermeticity evaluation proved DLC to be an excellent sealant of multilayered optical devices against moisture ingress and severe environments.

1. Introduction

The concomitance of infrared (IR) transparency and extreme hardness makes diamond-like carbon (DLC) films ideal for IR optical device applications. These films are typically characterized by their hard nature along with 'tunable' optical constants and chemical inertness. DLC films and related metastable phases are being synthesized by a variety of ion-based techniques such as D.C. plasma deposition, capacitively- and inductively-coupled nonisothermal R.F. plasma CVD, thermal R.F. plasma deposition, microwave plasma CVD, ion beam deposition, electron/laser/UV-assisted CVD and hollow cathode CVD.[1)–6)]

'Diamond-likeness' has been thought to be caused by ion-assisted compaction and the simulation of high pressure - high temperature conditions on an atomic scale, though the plasma is relatively cool. In some of these processes, additional mechanisms involving photons may also play an important role as some plasmas are known to be sources of intense UV radiation. Though there have been many reports on the optical and mechanical characterization of DLC films, there has been a lack of clear understanding of the films' applicability to IR optical devices.[7)–9)] This research places emphasis on this aspect and systematic studies elucidate the optically active and neutral roles of DLC.

2. Experimental

DLC films were prepared in an R.F. (13.56 MHz) asymmetric system and by D.C. plasma deposition. Precursors of various kinds like acetylene, benzene, acetone and n-butane were used and a range of process parameters were studied. In the D.C. plasma process, the substrates were held on a biased electrode in a high vacuum system. Problems of plasma sustainment due to carbon depositions on the electrical leads persisted, and this approach to DLC synthesis was abandoned after preliminary trials to characterize the films and to compare their properties with those of films prepared under R.F. conditions. The R.F. process was optimised as to the mechanistic details and the optimised parameters were utilized to generate DLC films on IR optics. Substrates like silicon, germanium, zinc sulphide, zinc selenide and quartz were cleaned by sonicating in acetone and 18 M ohm D.I. water prior to DLC deposition. All the DLC depositions were preceded by a sputter - etch step, to remove any remnant contaminants from the substrate surfaces, for periods of 5–20 minutes at self-bias voltages in the range of 400–600 V in an argon discharge sustained in the 10^{-3}–10^{-2} Torr pressure regime.

2.1 IR optical device development

A novel hybrid process of sputter deposition -

Science and Technology of New Diamond, edited by S. Saito, O. Fukunaga, and M. Yoshikawa, pp. 279–283.

be independent of the type of precursors, showing that though plasma-chemical reactions are present, they are not critical. The structural 'lost memory' effect was shown by earlier studies to result from impact-induced fragmentation of the energetic hydrocarbons at the growth surface, and our study confirms this observation.[9] The addition of hydrocarbons with higher penning ionization, such as benzene, helped in sustaining the plasma at larger cathode-to-anode spacings and lower hydrocarbon pressures. Inert gas additions reduced the deposition rates and thus, afforded control over the growth rate. Etchants like oxygen and air removed the film by the formation of volatile products, and this process allows the tuning of the thickness of the DLC films.

3.3 Film characterization

DLC film deposited on Si, Ge and quartz substrates were analysed for their structural and optical properties. Transmission electron microscopy showed a halo, indicative of an amorphous material. Scanning electron microscopy revealed no distinct surface morphology, indicative of a smooth surface.[10] DLC films on quartz substrates were analysed for UV-VIS absorption study and an optical bandgap in the range 0.72–1.73 eV was gleaned from Tauc analysis of the data. From the analysis of the optical absorption data, it was clear that the optical bandgap increased with increasing hydrogen concentration. Thus, the index of refraction decreases for films with greater bandgap. There has been a slight decrease in the refractive index for films thicker than about 100 nm, indicative of the 'snow pile' effect: the latest DLC to condense was less dense than the initial material deposited near the substrate interface. The refractive index varied between 1.9 and 2.25 under varying process conditions.

3.4 IR optical device applications

DLC films, being amorphous, do not contain grain-boundaries through which moisture might otherwise penetrate, leading to catastrophic failures of multilayered optical components. Thus, the films act as excellent hermetic sealants for optical devices in the infrared.

DLC as the low index (L) layer and Ge as the high index (H) layer in multilayer antireflection (AR) coating designs for 3–5 micron and 8–12 micron bands were experimentally realized, and the transmission spectra are depicted in Figs. 1 and 2. It is evident that DLC acts as an efficient and compatible material for multilayer design; these results are being reported for the first time.

Figure 3 shows a five-cavity quarterwave filter design with a thin (optically neutral) DLC on top of the stack to impart protection to the underlying film composite.

Figures 4 and 5 show the applicability of DLC as an optically neutral-hermetic sealant for the 10–12 micron and 14–16 micron IR bands. The reduced transmission from the theoretical value could be explained as due to the inherent absorptions of the substrate and the films.

Figure 6 clearly shows DLC as a replacement of an optically equivalent ZnS layer; i.e., as a terminating layer. It is evident from Fig. 7 that the

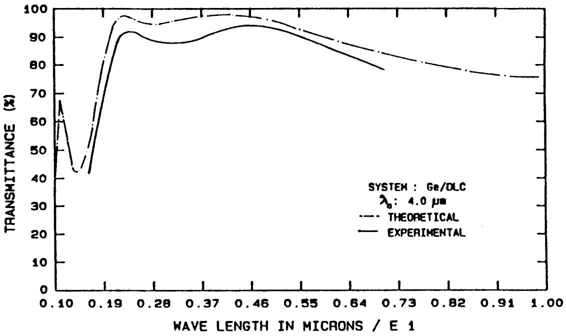

Fig. 1. Optimised antireflection (AR) design with Ge as H (n=4.0) and DLC as L (n=1.9) for the 3–5 micron band.

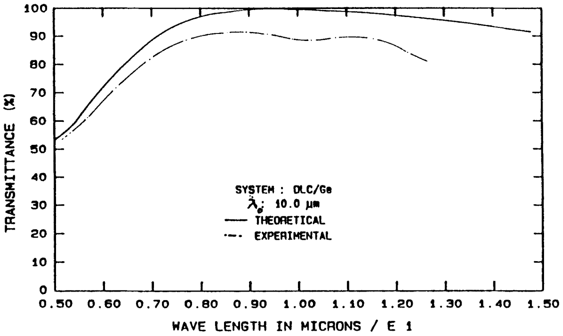

Fig. 2. Optimised AR design with Ge as H (n=4.0) and DLC as L (n=1.9) for 8–12 micron bands.

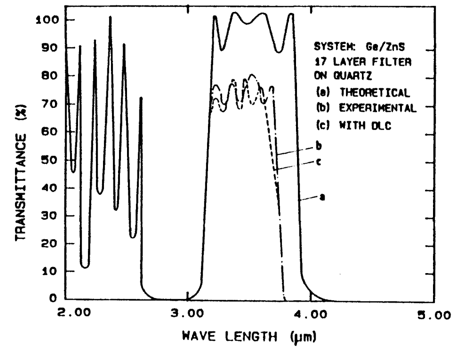

Fig. 3. Transmittance of a multiple half wave filter design: Air/HHLHLHHLHLHHLHLHHLHLHH/Quartz H=Ge (n=4.0); L=ZnS (n=2.35); Quartz substrate (n=1.52); λ_0=3.5 μm. (a) Theoretical. (b) Experimental. (c) Experimental with DLC 40 nm thick.

growth of DLC can be promoted on the ZnS layer by the use of a thin binder layer, thus affording a means of 'sealing' an IR optical device.

The DLC-based IR optical devices survived very stressing environmental and durability tests. Thermal conductivity measurements showed that DLC-coated IR optics had at least two to three orders higher thermal conductivity than conventional coatings, and this result has important implications for sensor system designs.

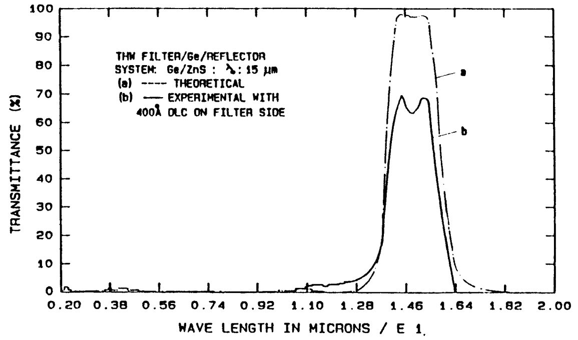

Fig. 5. Transmittance of a composite stack for 14–16 μm band. Design: HHLHLHHLHLHHLH/Ge/(0.5L H 0.5L)^{14}L H=Ge (n=4.0); L=ZnS (n=2.1); Ge Substrate (n=4.0). (a) Theoretical. (b) Experimental with 40 nm thick DLC protective layer on filter.

4. Conclusions

Diamond-like films synthesized under R.F. conditions have been optimised for their applicability to IR optical device applications. Various system configurations have been experimentally realized for the IR bands with DLC as an optically active and neutral film. Environmental tests revealed the protection imparted by DLC to these devices.

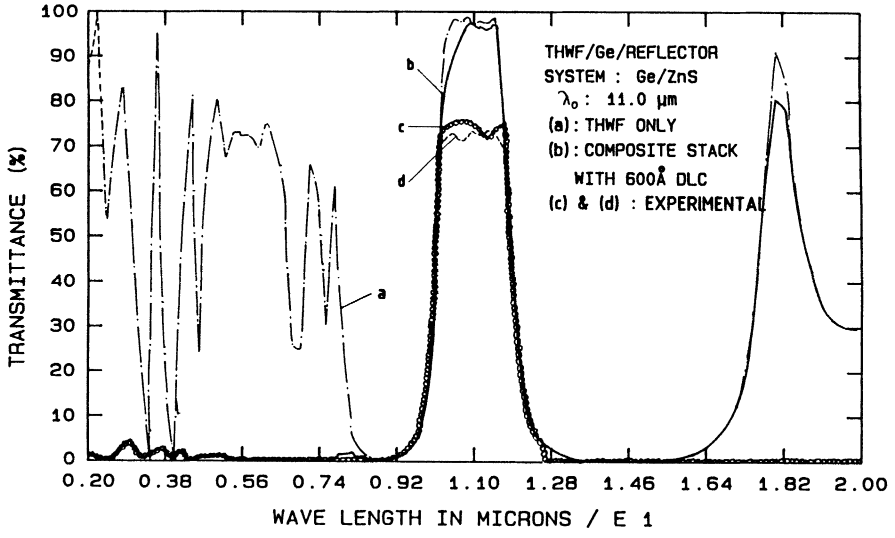

Fig. 4. Transmittance of a composite stack for 10–12 μm band. Design: HHLHLHHLHLHHLH/Ge/(0.5L H 0.5L)^{10}L H=Ge (n=4.0); L=ZnS (n=2.1); Ge Substrate (n=4.0). (a) Triple half wave filters stack only (theoretical). (b) Composite stack with 60 nm DLC (theoretical). (c) Composite stack without DLC (experimental). (d) Composite stack with 60 nm DLC (experimental).

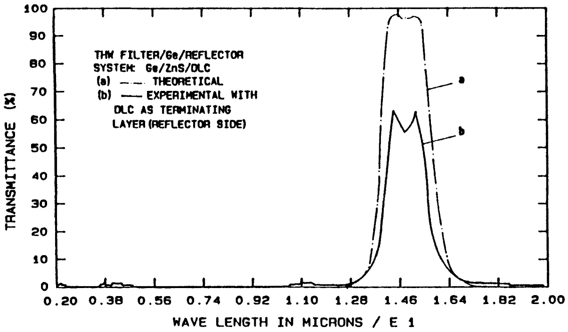

Fig. 6. Transmittance of a composite stack for 14–16 μm band. Design: HHLHLHHLHLHHLH/Ge/$(0.5L\ H\ 0.5L)^{14}L$ H=Ge (n=4.0); L=ZnS (n=2.1); Ge Substrate (n=4.0). (a) Theoretical. (b) Experimental with an optically equivalent DLC (n=1.9) terminating layer on reflector side.

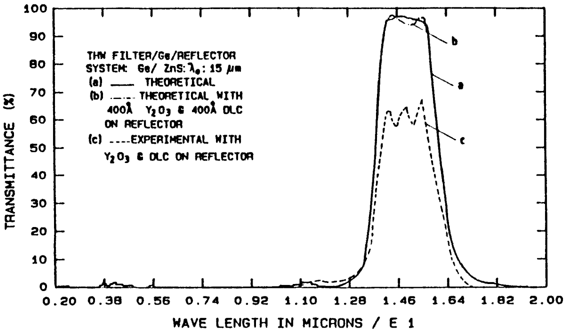

Fig. 7. Transmittance of a composite stack for 14–16 μm band. Design: HHLHLHHLHLHHLH/Ge/$(0.5L\ H\ 0.5L)^{14}L$ H=Ge (n=4.0); L=ZnS (n=2.1); Ge Substrate (n=4.0). (a) Theoretical. (b) Theoretical with 40 nm of Y_2O_3 and 40 nm DLC on reflector. (c) Experimental with Y_2O_3 and DLC.

Acknowledgements. The authors wish to acknowledge the help of M. N. Annapurna and S. S. Bhat in the preparation of the manuscript. They would also like to thank T. K. Alex, Head, Sensor Systems Division and N. Pant, Director, ISRO Satellite Centre, for their kind encouragement throughout the course of this work.

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