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Pulsed laser deposition and characterization of diamond like carbon (DLC) films on germanium, silicon and glass substrates

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Pulsed Laser Deposition (PLD) technique has been employed to deposit Diamond Like Carbon (DLC) films with modified parameters on germanium, silicon and glass substrates. A target of graphite was ablated by pulsed laser of 355 nm at room temperature with high repetition rate of 30 Hz. At 300mJ laser energy, 30Hz rate, 20°C temperature and 3.8cm substrate to target distance, good adhesive properties of the DLC films deposited on three different substrates were occurred under the same environment. Intensities ratio I_D/I_G of the D (for disorder-induced mode) and G (for Raman-allowed graphite-mode) bands were determined. The increase in transmission was observed in near infrared (NIR) and far infrared (FIR) region after depositing DLC coatings on Ge and Si substrates. Atomic force microscopy (AFM) and x-ray diffraction (XRD) were used for the study of surface morphology and structural properties. Various physical properties were determined.

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Keywords: PLD, DLC, Optical coatings, Raman spectroscopy, Band gap

1. Introduction

For many decades, thin film researchers and investigators have been involved in developing new deposition techniques and their characterization. Especially in FIR region materials are soft and also hygroscopic. During the years, PLD [1-4] has emerged, not only as a versatile deposition technique but also has advantages over other techniques in many ways. Deposition of good amorphous carbon (a-C) or DLC coating is one of the methods to protect the soft hygroscopic material surfaces. It has a broad transparency region which extends from NIR to FIR region. Researchers have deposited a-C films by many methods [5-7] and also utilized at commercial levels. However, PLD is one of the promising techniques which is also used to deposit DLC films with excellent stoichiometric ratios. DLC films have attained substantial attention recently due to the wide spectrum of potential applications [7]. Mainly, in mechanical applications which take advantage of the high mechanical hardness, low friction, optical transparency and chemical inertness of the material, due to the presence of C-C sp^3 bonds. The electrical properties are mainly dependent on the sp^2-bonding, while the sp^3-bonding determines the mechanical properties.

The main applications of DLC films are protective coatings of razor blades, hard disc drives in personal computers and anti-reflection coatings for IR windows.

Present study encircles the deposition and characterization of DLC films by PLD technique using high power density 3rd harmonic Nd: YAG laser and graphite (99.999% C) as a target material on Ge, Si and glass (Soda lime) substrates. Pang et al. [3] have prepared DLC films using laser wavelength of 355 nm at 5 Hz, while this paper contains DLC films on three different substrates at 30 Hz at the same wavelength. Characterization in terms of transmission (%T) in IR region, resistivity, film thickness, hardness, refractive index, extinction co-efficient, absorption co-efficient and band gap of deposited DLC films were reported. Raman scattering was done which determined the amorphous nature of carbon films. XRD was used to understand the film morphology. AFM was employed for surface profiling. Coatings on Si and Ge substrates were deposited in order to enhance the transmission in NIR and FIR region.

2. Experimental

The deposition and the analysis of the DLC films were carried out in a system designed and constructed in our laboratory. The substrates used for the growth of DLC film were Ge, Si and soda lime glass. Ge and Si substrates were taken from single crystals of these materials which were self grown by Czochralski technique in the induction furnace (BCG 365 Cambridge Instruments U.K.). The growth was performed in a vacuum~ 10^{-5} mbar. Single crystal seeds used for growth of Ge and Si crystals had [111] and [400] orientations respectively. The discs were cut perpendicular to the growth axis of the crystals and grinded using the Silicon Carbide abrasive down to 600 meshes. Both the surfaces of discs were mechanically polished using 1μm size alumina powder for Ge and Si. The finished thickness of Ge substrate was 2-3mm and in case of Si 0.5-0.8 mm. The glass substrate used was a soda

lime glass (n =1.52 at 546 nm) supplied by Menzel, Germany.

The pulsed laser deposition was performed with a Q-switched 3rd harmonic Nd:YAG laser (Spectra Physics) at 355 nm wavelength, average pulse energy: 300 mJ/pulse, power density: $2x10^9$ w/cm^2, fluence: 20 J/cm^2, pulse duration: 10 ns, laser beam diameter: 10 mm and 30 Hz repetition rate.

The experimental arrangement is shown in the Fig. 1. The laser pulses were focused on the rotating target (PT grade graphite supplied by Le Carbon-Lorraine, France) through a quartz lens with a focal length of 30 cm. The ablation target was in the form of a circular disc of 50 mm diameter and 10 mm thickness. The incidence angle to the graphite target was 45 degrees. The focused spot size on the target was about 1.5 mm^2 and average out put energy was 300 mJ/pulse. The distance between substrate and target was kept at 3.8 cm. The vacuum chamber was subsequently evacuated down to 4.0×10^{-6} mbar. The target and substrate holder was rotating with a speed of 4 rpm and 6 rpm respectively during deposition. The plasma plumes moved towards the substrates simultaneously which were parallel to the target. The substrates were kept at room temperature during deposition.

The optical properties of DLC films such as refractive indices (n) and extinction-co-efficient (k) were measured in visible wavelength region by using Ellipsometer (SE-850, SENTECH) and absorption co-efficient (α), optical band gap (E_g), real dielectric constant (ε_1) and imaginary dielectric constant (ε_2) were also calculated.

Transmission (%T) of DLC film was measured in the infrared region by Perkin Elmer FTIR spectrum 2000. This system is used to obtain the IR spectra of the samples.

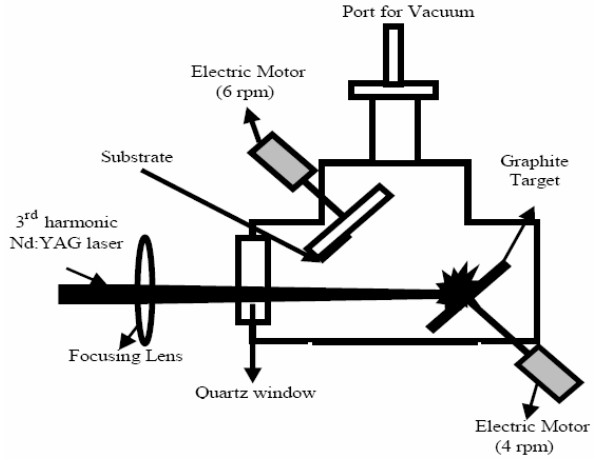

Fig. 1. Experimental setup of laser deposition.

Hardness on Moh's scale was checked. This scratch hardness test was done by hardness pencils supplied by Tricons Ltd. UK. The hardness of a material is a measure of how tightly the atoms are held together within it. This test is done by scratching one substance with another and using the Moh's Scale [8], which measures the relative hardness of various substances. It uses ten reference minerals. The hardness of a substance is determined by scratching it against a reference mineral. If it scratches that mineral, then it is of equal hardness or harder than that mineral, otherwise it is softer than that mineral. On the Moh's Scale diamond is ranked 10 and graphite is ranked between 1 and 2. Therefore, hardness of diamond is 40 times harder than the graphite.

The resistivity was measured for the films grown on glass substrate using the four-point probe technique. The instrument has four probes with sharp tips and 1mm probe spacing (Signatone U.S.A). The Si and Ge substrates were more conductive than the DLC films, so, resistivity measurements were not made for films grown on Si and Ge.

Film thickness was measured by using two instruments: Ellipsometer (SE-850, SENTECH) and digital film thickness monitor (FTM5 by Edward). The film thickness monitor FTM5 measures film thickness and deposition rate using the well-established quartz crystal micro-balance technique during deposition. The percentage error of FTM5 is about ±10% while Ellipsometer shows ±2% error.

The structural information of DLC films was obtained using Raman spectroscopy (M/S Avantes Raman). In the Raman spectrometer, a fiber optic probe is utilized to illuminate a sample with laser (785 nm) light and collect the Raman shifted light scattered from the sample. The Raman shifts of the scattered photons are produced as a result of vibrational energy transitions of the particular molecular species involved.

The morphologies of DLC films have been determined by easy Scan E-AFM Cantilever: micro fabricated silicon cantilever with integrated tip, 450 μm long and 50 μm wide. E-AFM system consists of Computer and Cantilever with deflection measurement system for scanning the samples. The easy Scan E-line atomic force microscope (E-AFM) can be used in the static force (contact) operating mode. In the static force operating mode, the cantilever bending due to the force acting on the tip is measured using a laser beam deflection system.

The XRD spectra of deposited DLC films on three substrates were taken by D-8 (Discover) X-ray diffractometer with KFLCu2K x-ray tube and scintillation counter detector. This is computer controlled and thus used for automatic operation.

3. Results and discussion

3.1 Visual inspection on DLC films

The film's colour appears to be golden and looks smooth. The results of adhesion, abrasion and temperature/humidity tests are shown in Table 1 (As per MIL-C-675C). No deterioration of the films under these tests was observed indicating that the films have good adhesion and high resistance to abrasion, temperature and humidity effects. The laser wavelength and substrate temperature affects the adhesion of DLC film. Usually,

lasers with short wavelength (UVregion) are preferred because at shorter wavelengths, the reflectivity of materials is much lower than at long infrared wavelengths and the laser beam is highly absorbing in the UV region.

Table 1. Specifications for testing dielectric coatings as per MIL-C-675C.

S. No.	Type of test	Basic technique	Results
1	Peel-off test	Scotch tape test	No deterioration
2	Abrasion test	40 strokes, Pressure 2.5 psi	No deterioration
3	Temperature/High humidity	T=40 ^{o}C	No deterioration

3.2 Physical properties

The resistivity of the grown DLC films is $9.4x10^4$ Ω-cm which lies within the range found in the literature [2,9].This high resistivity value ensures that the films is highly stoichiometric.

The hardness of DLC films was measured by using the Moh's Scale. Hardness of polished Ge, Si and glass substrates are reported to be 5, 7 and 6 respectively on Moh's scale [10] whereas the hardness of all these three DLC coated substrates is found to be 7. This test shows that our DLC films are harder on this scale.

The physical thickness of the film measured at the average rate of (0.04 - 0.11 nm/sec) 0.07 nm/sec by using the quartz crystal monitor was about 117 nm but with the ellipsometer, physical thickness on Ge, Si and glass was measured to be 79 nm with 11.7% voids concentration, 78 nm with 2.4% voids concentration and 115 nm with 18.8% voids concentration respectively which are within the error limits of the instrument. These results show that the film thickness is almost same on Ge and Si substrates. It is also noticed that film thickness is less on Ge and Si samples due to their position on the periphery of the substrate holder, while the film thickness on glass substrate is larger due to its central position at the substrate holder.

3.3 Optical properties

The optical properties of DLC films made on different samples such as refractive indices (n), extinction-co-efficient (k), absorption co-efficient (α), Optical band gaps (E_g), real dielectric constant (ε_1) and imaginary dielectric constant (ε_2) [11] were determined in the visible wavelength region.

The absorption co-efficient (α) of films were calculated using the well-known relation [9]

$$\alpha = 4\pi k/\lambda \quad (4)$$

where λ is the wavelength.

The measured band gap depends not only on the material but also on its characteristics such as crystallinity and stoichiometry. The diamond lattice type group IV semiconductors C, SiC, Si and Ge exhibit an indirect band gap with the conduction band minimum out side the Brillion zone center [12].

The band gap, determined using the well known dependence, for indirect band gap is $(\alpha\ h\nu)^{1/2} \sim (h\nu\text{-}E_g)$, Where E_g is the optical band gap, α is the absorption co-efficient and hν is the energy of the incident photon. By extrapolating $(\alpha\ h\nu)^{1/2}$ vs. the incident photon energy (hν) plot, the band gap could be obtained.

The energy band gap of films on glass, Ge and Si contains 1.14, 1.27 and 1.28 eV respectively. These results give information that more sp^2 site distortions causes the band gap to decrease on glass and energy band gap of films shows similarity for Ge and Si substrates and are comparable with the literature [1,2,6]. The shifting of the low energy band gap towards the low energy region could be associated to the introduction of the impurity level between the conduction band and valence band.

The high refractive index on substrates as predicted in (Table 2) was attributed to a lack of incorporation of hydrogen into the films. A higher index of refraction usually indicates DLC with higher hardness and better wear resistance. The optical properties results of each sample are summarized in Table 2.

Table 2. Optical parameters of DLC films.

Substrates	Refractive index (n) at 632.8 nm	Extinction coefficient (k)	Absorption coefficient α (cm^{-1})	Band gap (E_g) (eV)	Real dielectric constant (ε_1)	Imaginary dielectric constant
Ge	2.53	0.2041	5.02×10^4	1.27	6.36	1.03
Si	2.34	0.1990	4.90×10^4	1.28	5.44	0.93
Glass	2.43	0.4687	1.15×10^4	1.14	5.68	2.28

Figs. 2 to 4 represent the results of transmission in the IR region (1.3 – 25 μm) of uncoated and coated substrates which show flat curves in this region.

An increase in %T of DLC coated Ge and Si samples were observed and decrease in %T was measured in case of coated glass sample. The maximum %T increased in coated Ge sample at 2 μm is about 12% (Fig. 2.)

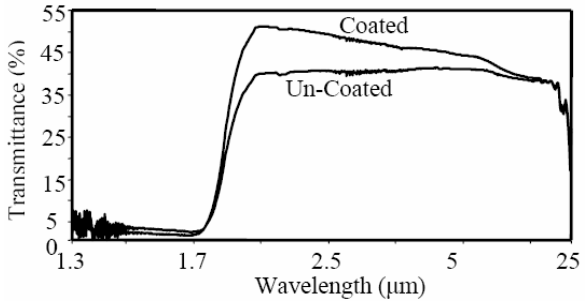

Fig. 2. Transmission curve of DLC coating on Ge substrate.

In case of coated Si sample it is ~ 5% at 1.8 μm (Fig. 3.). This increase in %T results due to low refractive index of film than that of Ge and Si substrates. On the other hand a decrease in %T in coated glass (Fig. 4.) is resulting from a higher refractive index of the film than that of the glass substrate.

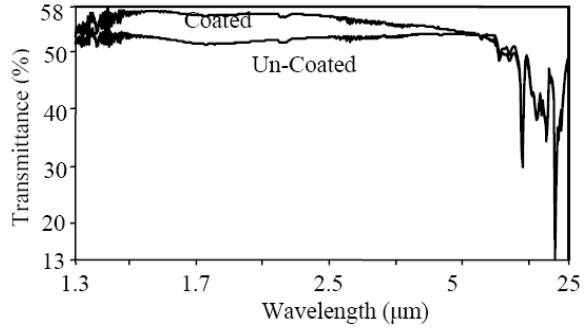

Fig. 3. Transmission curve of DLC coating on Si substrate .

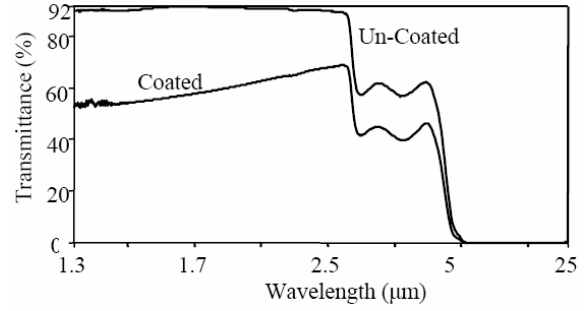

Fig. 4. Transmission curve of DLC coating on glass substrate .

3.4 Raman spectroscopy

Raman Spectroscopy is based on the inelastic scattering of photons in the optical range of lattice vibrations. Raman spectra are sensitive to changes in translational symmetry and can be used to study disorder, formation of crystallites, or changes in structure of DLC films. An important parameter characterizing the Raman spectra of these materials is the ratio of intensities of the D and G bands, I_D/I_G, which may be related to the degree of disorder of the graphite structure. Correlations of I_D/I_G with other parameters were found in a-C films. Cho et al. [2] observed that the decrease of I_D/I_G is accompanied by an increase of electrical resistivity, optical band gap, hardness and mass density. Tamor and Vassell [2] pointed out that the increase of the G band width correlates with an increase of hardness and density.

The intensity versus frequency spectra of our DLC films on various substrates are depicted in Figs. 5, 6 and 7. In these figures the frequency is plotted relative to the laser frequency, so the frequency scale represents the Raman shift.

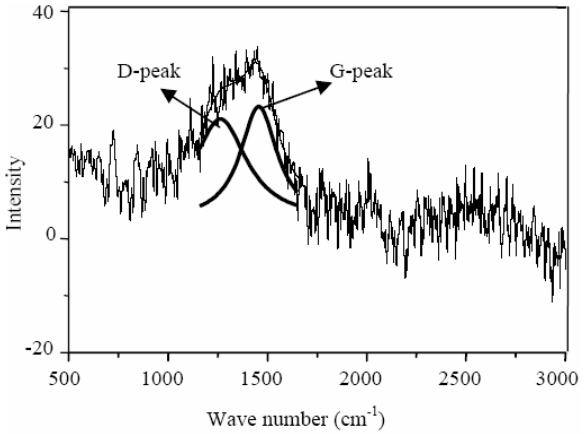

Fig. 5. Raman spectra of DLC film on Ge substrate.

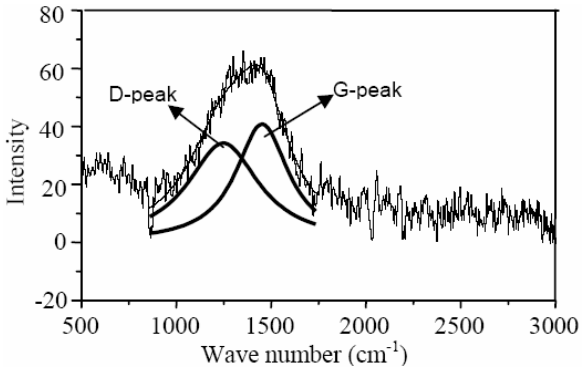

Fig .6 Raman spectra of DLC film on Si substrate.

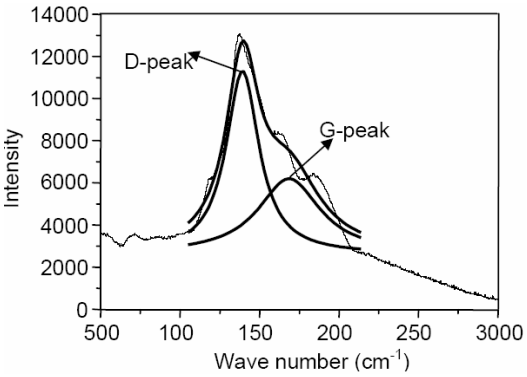

Fig .7. Raman spectra of DLC film on glass substrate .

The results from Raman spectra such as G peak position and I_D/I_G ratio intensities are summarized in table 3. Spectra were measured in the range from 0 to 3039 cm^{-1}. The G and D-peaks from our spectra were fitted with Lorentzian line shapes to quantify their respective FWHM. It was noticed that there were two peaks in our spectra, one in the range of 1248 cm^{-1} to 1385 cm^{-1} and the other in the range of 1452 cm^{-1} to 1602 cm^{-1} which shows that these films are a-C. It was also found that shift of Raman G-peak of films on Ge and Si substrates towards lower wave number gives information about larger concentration of sp^3 and on glass it shows more sp^2 concentration [6]. The Raman test shows that the film's spectra are similar and have the typical character of DLC Raman spectrum.

Table 3. The Raman characteristics of DLC films on various substrates.

Substrates	G-peak centre (cm^{-1})	G-peak FWHM	D-peak centre (cm^{-1})	D-peak FWHM	I_D/I_G
Ge	1457.3	225.59	1264.4	322.04	1.26
Si	1452.7	338.42	1248.2	458.3	1.14
Glass	1685.3	476.08	1392.5	250.69	1.28

3.5 Surface morphology

Sample structure images are shown in Fig. 8 (a), (b), (c) with surface morphology of a DLC film on different substrates as viewed from the top. The average roughness on a DLC film surface of 77x77 μm^2 for Ge, Si and glass substrates are 4 Å, 5 Å and 4 Å respectively. AFM results show that the average roughness of DLC films measured is comparable to the results given in literature [4].

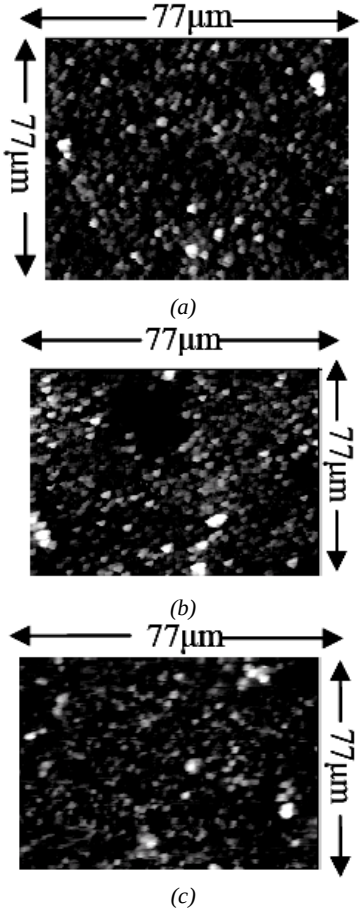

Fig. 8a) AFM image of DLC film on Ge substrate b) AFM image of DLC film on Si substrate c) AFM image of DLC film on glass substrate.

3.6 XRD spectra

The XRD spectra of deposited DLC films on three substrates are analyzed in Fig. 9 (a), (b) and (c). Coating and measuring conditions are same on different substrates. Glass, Ge and Si substrates used in this experiment are amorphous, single crystal [111] orientation and single crystal [400] orientation respectively. Some additional characteristic peaks are observed in the curves of Ge and Si. XRD results evaluated that films are crystalline on Ge and Si substrates but amorphous on glass. Two peaks are evaluated on Ge substrate, one is at $2\theta=44.2^0$ and assigned to diamond peak (cubic structure and face centered) and other is $2\theta=38^0$ and related to $C_6CH_4CH_2C_6H_4$ peak (orthorhombic structure and primitive). But some part of spectrum i.e. 45^0-50^0 also gives information about amorphous structure. Similarly, on Si substrate, peak at $2\theta=28.2^0$ which is assigned to Quinquephenyl ($C_{30}H_{22}$) peak (monoclinic structure) and other is at $2\theta=29.5^0$ which is related to $(C_6H_{10})_n$ peak. The behavior of XRD spectrum on glass shows that structure of film is amorphous.

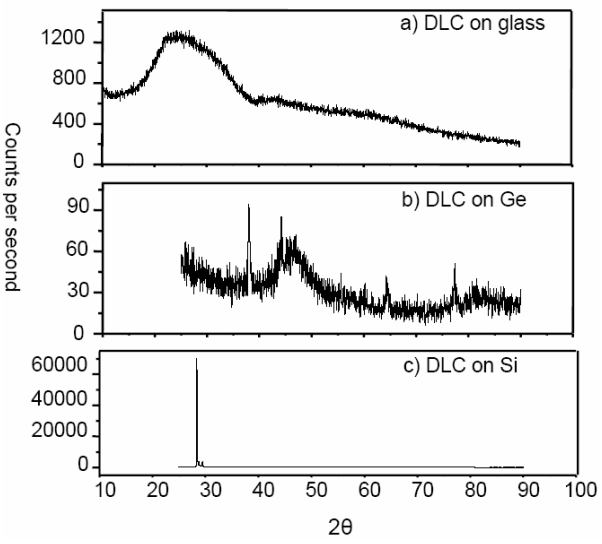

Fig. 9. XRD curves of DLC films on a) glass b) Germanium c) Silicon substrates.

4. Conclusions

It is concluded from our investigations that the DLC films deposited simultaneously on Ge, Si and glass substrates by PLD technique at high repetition rate of 30Hz. Different physical and optical properties of films were studied. We also observed hard coatings of DLC on three substrates when ablated with 3rd harmonic Nd: YAG laser (355nm) at room temperature. The resistivity of films was found to be about $9.4x10^4$ Ω-cm. Larger film thickness was noticed i.e. 115nm on glass substrate due its central position on substrate holder as compared to on Ge and Si substrates which was measured to be 79 nm and 78 nm respectively. The absorption edge of DLC films was shown to exhibit an indirect band gap like behavior. These films obtained energy band gap of about 1.14-1.28 eV. A higher refractive index was achieved which usually indicates DLC with higher hardness and better wear resistance. The average roughness on a DLC film surface of 77x77 μm^2 for Ge, Si and glass substrates are 4 Å, 5 Å and 4 Å respectively. From Raman spectra, greater sp^3 concentration of film was noticed on Ge and Si substrates due to shift of Raman G-peak towards lower wave number and larger sp^2 concentration on glass substrate. XRD results evaluated that films are crystalline on Ge and Si substrates but amorphous on glass. The application of DLC films seems very attractive to enhance the transmission of Ge windows and lenses in mid and far IR regions. We found about 12% increase in transmission at 2 μm on Ge substrate whereas about 5% at 1.8 μm in case of Si substrate. The experiment was performed many times and with these parameters, hard films are obtained. The next step in our research will be the improvement of film thickness and to enhance the transmission more in FIR region on Ge and Si substrates.

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