

Formation of Silver Implanted Polycarbonate Nanocomposite by One Year Ambient Temperature Annealing

*Suman Bahniwal^a, Anita Atwal^a
Annu Sharma^b, Sanjeev Aggarwal^b

^aBPSIHL, Bhagat Phool Singh Mahila Vishwavidyalaya, Khanpur Kalan, Sonapat

^bDepartment of Physics, Kurukshetra University, Kurukshetra

Abstract

Silver-polycarbonate nanocomposites have been synthesized by implanting different doses of silver ion in the 250- μm thick specimens of polycarbonate followed by one year ambient temperature annealing. Optical absorption, transmission and reflection spectra of the implanted polycarbonate specimens after annealing were measured by UV-Visible Spectroscopy in the range from 190 nm to 900 nm. The surface plasmon resonance (SPR) peak appears in absorption spectra of implanted polycarbonate specimens after annealing confirmed the formation of silver nanoparticles and shift of the peak position & increase in intensity is observed as the size of nanoparticles is increases with increases dose. From the UV-Visible spectra, band gap and optical constant such as refractive index, extinction coefficients were determined. The increment in the value of refractive index from 1.51 (virgin) to 2.56 (implanted polycarbonate) after annealing of one year ambient temperature can be utilised as a useful material for waveguide fabrication.

Keywords: Polymers-Nanocomposites, Ion Implantation, UV-Visible Spectroscopy, Optical Constants, Waveguide.

Introduction

Metal-polymer nanocomposites are promising candidates for wide range of fields including electronics, photonics, plasmonics and

sensing [1-4] because of their unique optical properties, large third order optical nonlinearity and fast time response as compared with metal-polymer composites. In metal-polymer nanocomposites, very small metal particle size enhances the properties while the polymer matrix materials will act to stabilize the particle size and growth besides providing the required transparent medium. The various approaches such as vapour phase co-deposition [5], ball milling [6] and sol-gel processing [7] had been used in order to improve the properties of polymers. Now a day, Ion implantation becomes a very convenient method for the formation of metal polymer nanocomposite because of its intrinsic ability in controlling the type, concentration and spatial location of the metal dopant [8-9]. The high value of the metal volume fraction inside an insulator results in useful improvement in optical properties like refractive index and dielectric function of composite [10]. In polymers, however, it has been found that the major change in refractive index occurs in the region of the electronic energy loss of the implanted ions causing high refractive index zones in the surface [11]. This high refractive index zone can be useful for waveguide application. Optical waveguide is a basic element of a photonic integrated circuit. It consists of a high refractive index guiding layer, sandwiched between two lower-index cladding layers. The optical signal travels in the guiding layer and is confined in the transverse directions as a result of total internal reflection at the interfaces between core and cladding [12-14].

In the present work, we have studied the optical properties of silver polycarbonate nanocomposites synthesized by implantation followed by annealing and the calculated optical parameters would be helping the researchers towards applying polymers in optical device like optical waveguide.

Experimental

The polycarbonate specimens of area $2 \times 2 \text{ cm}^2$ were cut from the 250 μm thick, commercially available and optically transparent sheet. Specimens were implanted with 1MeV Ag^+ ions to various doses ranging from 1×10^{15} to 5×10^{16} ions/ cm^2 at a beam current density was $\sim 1 \mu\text{A}/\text{cm}^2$ under a vacuum of $\sim 10^{-7}$ Torr, to prevent thermal degradation of the polymer specimens. Now the implanted specimens were annealed for one year ambient temperature. The optical absorption, transmission and reflection measurements were performed on virgin and implanted specimens after annealing using a Shimadzu Double Beam Double monochromator Spectrophotometer (UV-2550), equipped with Integrating Sphere Assembly ISR-240A in the wavelength range of 190nm to 900nm with a resolution of 0.5nm. All the spectra were recorded keeping air as the reference. From the UV-Visible spectra, optical parameters like band gap, refractive index and extinction coefficient were calculated.

Results and discussions

UV-Visible absorption spectra of virgin and silver implanted polycarbonate specimens after annealing of one year ambient temperature are displayed in Fig.1 (a). In case of silver implanted polycarbonate specimens without annealing, no indication of the SPR peak was observed. Only the fundamental absorption edge of virgin polycarbonate near 300 nm shifts towards higher wavelengths and simultaneously edge flattens with increasing the implantation dose and the optical intensity increases continuously with silver ion implantation dose. This increase in absorption and red shift of the absorption edge may be arises due to the original bonds in the polymer are ruptured leading to chain scission, free radical formation, cross linking, resulting in the formation of new bonds and results

are accepted in J. Macr. Sci. Phys. [15]. But after the annealing of one year ambient temperature the SPR absorption peak is observed in visible region due to reduction of Ag^+ to Ag^0 atoms and Ag^0 combines with Ag^0 , hence the occurrence of selected peak in the absorption can corresponds to beginning of the formation of silver nanoparticles inside the polycarbonate specimens. The dispersed isolated silver ions and atoms do not exhibit such absorption in the visible range before annealing.

For the lowest dose of the order of 1×10^{15} ions/cm² (curves b, Fig. 1(a)) a weak SPR absorption peak near to 490 nm is observed and then increase of the dose of the order of 5×10^{15} ions/cm² (curves c, Fig. 1(a)) peak intensity increases and shifted to 540 nm & further increases of the dose of the order of 1×10^{15} ions/cm² (curves d, Fig. 1(a)) there is the shifting of the peak position 560 nm is observed. At a maximum dose of the order of 5×10^{16} ions/cm² (curves e, Fig. 1(a)) there is the further shifting in the peak position nearer 580 nm with some peak broadening significantly is observed. These absorption peaks at different wavelengths are fitted to a Gaussian curve for the calculation of a full width at half maximum (FWHM).

The size of nanoparticles is calculated by the formula [16]

$$d = (2hv_f / \Delta E_{1/2}) \text{-----} (1)$$

where d is the diameter of the nanoparticles, v_f (1.39×10^6 m/s) is the Fermi velocity of electrons in bulk silver, h is Planck's constant, and $\Delta E_{1/2}$ is the FWHM of the absorption peak.

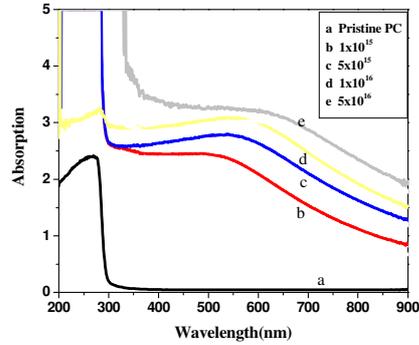


Fig.1 (a)

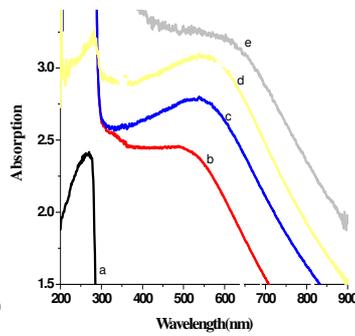


Fig.1 (b)

Fig.1 (a, b) UV-Visible absorption spectra of the silver implanted polycarbonate after annealing of one year ambient temperature

The above equation is valid as long as the silver nanoparticle dimension is smaller than the mean free path of the electrons in the bulk metal. The mean free path of electrons is about 27 nm at room temperature for bulk silver. Using Eq.1, the size of the silver nanoparticles at 1×10^{15} , 5×10^{15} , 1×10^{16} and 5×10^{16} ions/cm² have been found to be 1.84, 2.18, 2.20 and 2.30 nm respectively.

Similar types of red shift of SPR peak for different particle sizes, as is observed in Fig. 1(a), have been reported for other metal nanoparticles/dielectric systems [17-19]. The shift of the SPR peak position observed in the present study is probably not only due to the change of the size of the silver nanoparticles. The present technique leads to a simultaneous increase of the metal volume fraction with increasing size of the Ag nanoparticles [20]. The volume fraction of the metal particles can be determined from the Maxwell Garnett equation

$$\epsilon_{Ag}(\lambda_p) = (2+f/1-f) \times n^2 \text{-----} (2)$$

$\epsilon_{Ag}(\lambda_p)$ is the value of the real part of the dielectric function of bulk silver at the wavelength λ_p of the maximum of the absorption of the

SPR and n is the refractive index of the polymer. The dielectric function A_g in this study from the values of the refractive index and extinction coefficient found experimentally [21].

Metal volume fraction is increases from 0.66 at lower dose to 0.72 at higher dose. Since the changes in the metal volume fraction of nanoparticles in the matrix leads to a change of the dielectric constant of the nanocomposite due to electromagnetic interaction between neighbouring particles, this effect is also thought to be responsible for the shift of the SPR peak as has been shown previously for Au nanoparticles in a nylon 11 matrix. Therefore, it seems likely that the observed changes in optical absorption spectra for the silver nanoparticles can be qualitatively explained by the changes in the effective dielectric constant of the silver-polycarbonate nanocomposite due to changes in size and metal volume fraction in the polycarbonate matrix.

In order to determine the optical band gap of the silver-polycarbonate nanocomposite, the absorption coefficient (α) was calculated from the absorbance spectrums using the formula:

$$(\alpha) = 2.303(A / d) \text{ ----- (3)}$$

where d is the film thickness and A is the optical absorbance.

For the determination [22-23] of optical band gap, $(\alpha h\nu)^{1/2}$ was plotted as a function of photon energy $h\nu$, taking into account the linear portion of the fundamental absorption edge of the UV-Visible spectra (curves a-e in Fig. 2). From the intercept (extrapolations) of the best fit lines (Fig. 2) on $h\nu$ axis, optical band gaps have been determined for virgin and implanted polycarbonate and the results are presented in Table 1. The determination Coefficient R^2 has been found to be greater than 0.99 for the fitted lines (Fig. 2). A decrease in optical

band gap from 4.1 eV (Virgin) to 2.94 eV (at a dose of $3 \times 10^{16} \text{ Ag}^+ \text{ cm}^{-2}$) has been observed. This reduction in band gap continuously with increasing dose is found due the increasing of the metal volume fraction in the polycarbonate matrix.

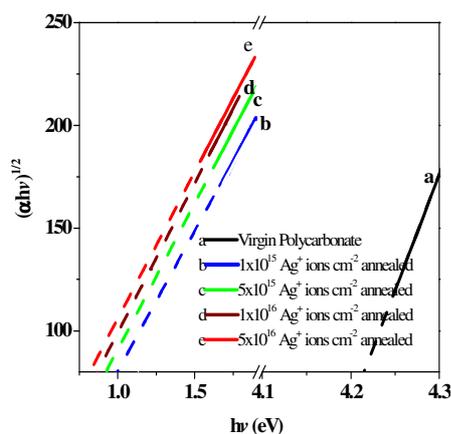


Fig.2 The plots of $(\alpha hv)^{1/2}$ vs. photon energy (hv) implanted and unimplanted films

Table 1.

S. No.	Implanted dose	Optical band gap E_g (eV)	Regression coefficient 'R'	Metal volume fraction(f)
1	Virgin	4.10	.99	--
2	1×10^{15}	3.50	.99	.66
3	5×10^{15}	3.48	.99	.68
4	1×10^{16}	3.16	.98	.70
5	5×10^{16}	2.94	.99	.72

A sharp change in color of the implanted polycarbonate specimens from transparent (Virgin) to brown (at a dose of $5 \times 10^{15} \text{ ions/cm}^2$) and finally dark brown at highest implantation dose (of $5 \times 10^{16} \text{ ions/cm}^2$) is observed. This change in color is also apparent from the transmission behavior as shown in Fig. 3. The change in color can be due to presence of silver nanoparticles or formation of color

sensitive conjugated bonds with loosely bound π -electrons which can easily be excited by the visible photons leading to observed change in color of the implanted surface. The transmission spectra the virgin polycarbonate (curve a, Fig.3) shows constant transmission of $\sim 90\%$ in the visible region and decreases at 300nm. After silver ion implantation with 1×10^{15} ions/cm² (curve c, Fig.3) it falls abruptly to 15% at 900 nm and then decreases continuously up to 1% at 300nm. At highest dose of the order of 5×10^{16} ions/cm² (curve h, Fig.3) transmission falls to 1% at 900 nm and then decreases continuously zero at 300nm.

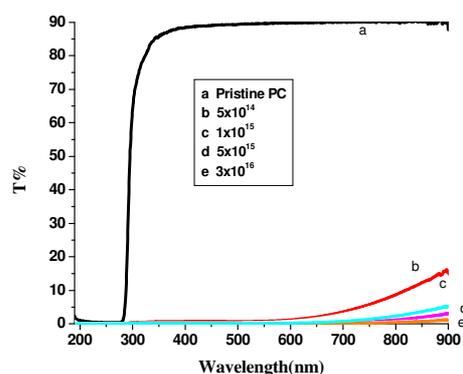


Fig. 3 UV-Visible transmission spectra of the virgin and silver implanted polycarbonate nanocomposite

The changes of the transmission and reflection are reciprocal. This test indicates that the decrease in the transmission of Ag^+ implanted PC may result not only from the increasing light absorption in polycarbonate, but also from the increased reflection from the polymer surface implanted. Fig. 4 Shows the UV-Visible reflectance spectra of virgin and silver implanted polycarbonate. The effect of Ag^+ ion implantation is sizable about 4 time's higher reflection at highest dose (curves *h*, Fig. 4) with respect to virgin polycarbonate. The enhanced reflectivity follows from the modification of the polymer surface by Ag^+ ion beam (24-26).

In general, the reflection spectra are related to the dispersion of the optical constants (refractive index n and extinction coefficient k) of the material. Also, the reflectivity is modulated by the optical phase change due to the presence of the modified layer created by the ion implantation beneath the surface of the material. The optical constants and their depth profiles in that layer within polycarbonate are functions of implantation ion energy and doses (27-29).

The complex refractive index characterizes the optical properties of any solid material. The complex refractive index of the matrix is expressed as

$$n^* = n + ik \text{ ----- (4)}$$

where n is the real part and k is the imaginary part of complex refractive index. The refractive index of the matrix can be obtained from the following equation [23]:

$$R = ((n - 1)^2 + k^2) / ((n + 1)^2 + k^2) \text{ ----- (5)}$$

$$n = (R+1/R-1) + \sqrt{(4R/(R-1)^2)-k^2} \text{ ----- (6)}$$

Where R is the reflectance and k is the extinction coefficient, given by the expression,

$$k = \alpha\lambda/4\pi$$

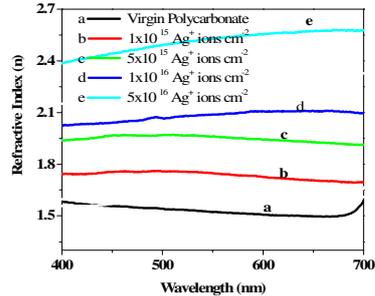


Fig. 4 a

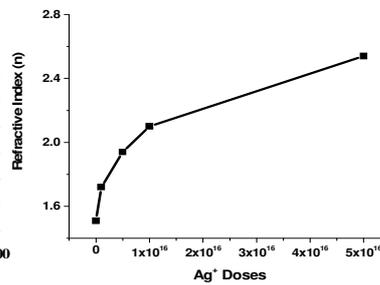


Fig. 4 b

Fig. 4 (a, b) Variation of refractive index verses wavelength and doses of virgin and silver implanted polycarbonate specimens at various doses.

Table 2

S. No.	Implanted dose	Refractive index (n)
1	Virgin	1.51
2.	1×10^{15}	1.72
3.	5×10^{15}	1.94
4.	1×10^{16}	2.10
5.	5×10^{16}	2.54

It is seen that the value of the refractive index of the polycarbonate increases with increases of the silver ion dose. The variations of the refractive index values at investigated wavelength range show that some interactions take place between photons and electrons. An increases in refractive index from 1.51 (Virgin) to 2.54 (at a dose of $5 \times 10^{16} \text{ Ag}^+ \text{ cm}^{-2}$) has been observed at 600 nm wavelength. This increase in value of refractive index is can be associated with the decrease in the fundamental band gap absorption.

Conclusion

We have prepared silver polycarbonate nanocomposite by ion implantation. Results of the UV-Visible observations revealed that SPR peaks occur in absorption spectra indicate the formation of metal nanoparticles in the polymer matrix. From absorption we have to calculate the band gap of the material. Reduction in the band gap is found due to increases in metal volume fraction of nanoparticles in the polymer matrix. The refractive index changes induced by implantation are also very large. These values show that silver implantation is suitable to change refractive index of polycarbonate

matrix and has a potential applicability for optical devices, e.g., optical waveguides and photo-optical switching devices.

References

- Nikolay A. Mirin, and Naomi J. Halas , Nano Lett., Vol. 9, No. 3, 2009.
- Tobias Holmgaard, Zhuo Chen, Sergey I. Bozhevolnyi, Laurent Markey, Alain Dereux, Alexey V. Krasavin, and Anatoly V. Zayats , Optics Express, Vol. 16, No. 18, 13586, 2008.
- Igoris prosy?evas1, judita puišo, asta guobien?, sigitas tamulevi?ius, ram?nas naujokaitis, , ISSN 1392-1320 Materials Science (Med • iagotyra). Vol. 13, No. 3. 2007.
- K. Lance Kelly, Eduardo Coronado, Lin Lin Zhao, and George C. Schatz , J. Phys. Chem. B, 107, 668, 2003
- S. Srivastava, M. Haridas & J. K. Basu, Bull. Mater. Sci. 31, 213-217, 2008.
- A. L. Stepanov, V. N. Popak, I. B. Khaibullin, U. Kreibig, Nucl. Instr. & Phys. Res. B 191, 473, 2002.
- Wu. Yuguang, Zhang Tonghe, Zhang Yawen, Zhou Gu, Zhang Huixing, Zhang Xiaoji, Surf. & Coat. Technol. 148, 221, 2005.
- A. L. Stepanov and I. B. Khaibullin, Rev. Adv. Mater. Sci. 9, 109, 2005.
- Sergey Sarkisov, Zedric Teague, Putcha Venkateswarlu, Hossin Abdeldayemb) and Donald Frazier Grigory Adamovsky , J. Appl. Phys. 81 (6), 2889, 1997.
- S. M. Kostritskii, P. Moretti , Journal of Applied Physics 101, 094109, 2007.
- J. R. Kulisch, H. Franke, R. Irmischer and Ch. Buchal ", J. Appl. Phys. 71, 3123, 1992.
- L. H. Slooff, A. Van Blaaderen, A. Polman G. A. Hebbink, S. I. Klink, F. C. J. M. Van Veggel, D. N. Reinhoudt and J. W. Hofstraat , J. Appl. Phys., 91, 3956 , 2002.
- U. Kreibig and M. Vollmer, Optical Properties of Metal-Clusters (1995) (Springer, Berlin)
- C. Ranganathaiah , High Performance Polymers", Vol. 18, No. 6, 933-947 (2006).

- C. Huang and C. Z. Yang, "Fractal aggregation and optical absorption of copper nanoparticles prepared by in situ chemical reduction within a Cu²⁺-polymer complex" *Appl. Phys. Lett.*, 74, 12, 1999
- R. Lamber, S. Wetjen, G. S. Ekloff, and A. Baalman, *J. Phys. Chem.*, 13834, 99 (38), 1995.
- A. L. Stepanov, R. I. Khaibullin, I. B. Khaibullin, *Philosophical Magazine Letters*, 77, 5, 261, 1998.
- K. Akamatsu, S. Deki, *J. Mater. Chem.* 7, 1773, 1997.
- K. Akamatsu, S. Takei, M. Mizuhata, A. Kajinami, S. Deki, S. Takeoka, M. Fujii, S. Hayashi, K. Yamamoto, *Thin Solid Films* 359, 55, 2000.
- M. D. Migahed, H. M. Zidan, *Current Applied Physics* 6, 91, 2006.
- P. B. Johnson and R. W. Christy, *Phys. Rev.*, vol. 6, 4370, 1972.
- Y. Deng, Y. Sun, P. Wang, D. Zhang, H. Ming and Q. Zhang, *Physica E*, vol. 40, 911, 2008
- K. Akamatsu, S. Takei, M. Mizuhata, A. Kajinami, S. Deki, S. Takeoka, M. Fujii, S. Hayashi and K. Yamamoto, *Thin Solid Films*, 359, 55, 2000.
- K. A. Bogle, S. D. Dhole and V. N. Bhoraskar, *Nanotechnology*, 17, 3204, 2006.
- S. Srivastava, M. Haridas and J. K. Basu, *Bull. Mater. Sci.*, 31, 213, 2008.
- M. Voué, N. Dahmouchène and J. D. Coninck, *Thin Solid Film*, 519, 2963, 2011,
- M. V. Fuke, A. Vijayan, P. Kanitkar, M. Kulkarni, B. B. Kale and R. C. Aiyer, *J. Mater Sci: Mater Electron*, vol. 10, p. 9787, 2008.
- H. Chen, T. Ming, L. Zhao, F. Wang, L. D. Sun, J. Wang and C. H. Yan, *Nano Today*, 5, 494, 1996, Z. Zhang, B. Zhao, and L. Hu, *J. Solid State Chem.*, vol. 121, p. 105, 2010.
- S. Novak, R. Hrach, M. Svec, V. Hrachova, *Thin Solid Film*, 519, 4537, 2011.