Synthesis of copper nanoparticles in polycarbonate by ion implantation

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Abstract. Copper nanoparticles have been synthesized in polycarbonate by 75 KeV Cu^- ion implantation with various doses ranging from 6.4×10^{15} to 1.6×10^{17} ions/cm^2 with a beam current density of 800 nA/cm^2. The composites formed were structurally characterized using Ultraviolet-Visible (UV-Visible) absorption spectroscopy. The appearance of particle plasmon resonance peak, characteristic of copper nanoparticles at 603 nm in absorption spectra of polycarbonate implanted to a dose of 1.6×10^{17} ions/cm^2, indicates towards the formation of copper nanoparticles in polycarbonate. Transmission electron microscopy further confirms the formation of copper nanoparticles having size ~3.15 nm. The formation of copper nanoparticles in the layers carbonized by Cu^- implantation has been discussed. The synthesized copper-polycarbonate nanocomposite has been found to be more conducting than polycarbonate as ascertained using current–voltage characteristics.

Keywords. Polycarbonate; nanoparticles; ion implantation; UV-Visible spectroscopy.

1. Introduction

Nanocomposite materials containing nanometer-size metallic particles embedded in polymers have recently generated increasing interest as advanced technological materials because they show attractive optical properties at the surface plasmon resonance (SPR) wavelength due to dielectric and quantum confinement effects. When these nanocomposite materials with certain metallic nanoparticles like copper, gold and silver are exposed to light they exhibit a strong absorption maximum, at a particular wavelength called the SPR wavelength, due to photon-induced oscillation of the electron charge density. Such pronounced resonance lines shown by noble-metal nanoparticles caused by collective excitations of conduction electrons are also known as particle plasmon resonance (PPR) or Mie plasmons (Kreibig and Vollmer 1995). In general, the band width, intensity and position of the PPR wavelength of these metallic particles vary with particle size and shape and with their surrounding matrix (Kreibig and Vollmer 1995; Beecroft and Ober 1997; Lance et al 2003). The sensitivity of the PPR frequency to small variations of these parameters can be used in various applications such as colour filters (Quinten 2000; Biswas et al 2004) sensors (Haes and Van

Duyne 2002; Haes et al 2004) and all optical switching devices (Stegeman and Wright 1990).

Probing the particle–matrix interface physics is not an experimentally easy task and little knowledge exists on the subject. On the other hand, the contribution of the particle–matrix interaction may be important for the tailoring of the material physical properties. As a consequence of small dimensions of nanoparticles, quantum-size effects arise which introduce changes in its optical properties compared to the bulk material. Because of the relatively large number of atoms that conforms a metallic nanoparticle and its shape, these quantum effects are difficult to calculate. Thereby, having experimental evidence of such effects is crucial in terms of volume concentration and their spatial distribution.

Several methods such as co-sputtering (Schurmann et al 2005), reduction of a metal salt (Troger et al 1997; Huang and Yang 1999) and ion implantation (Umeda et al 2003; Boldyryeeva et al 2005; Yuguang et al 2005; Teixeira et al 2009) are used to produce these composite systems. Among them, ion implantation stands out for its numerous advantages. Precise concentration control and in-depth dopant profiling is achieved by designing the implantation parameters, while surface localization is resolved using masks or focused ion beam techniques. These possibilities are particularly important for the application of the technique of ion beam synthesis to produce new compounds and different phases in the irra-

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diated polymer surfaces, yielding new interesting properties, by implanting ions of various chemical elements (Umeda *et al* 2003; Boldyryeeva *et al* 2004; Stepanov 2004; Takeda *et al* 2004; Boldyryeeva *et al* 2005; Yuguang *et al* 2005; Srivastava *et al* 2008; Teixeira *et al* 2009).

In the present work, copper nanoparticles have been synthesized inside the polycarbonate matrix by low energy ion implantation and their effects on optical as well as electrical properties have been discussed. Polycarbonate was chosen as the polymer matrix because it is highly transparent in the visible spectral range, which makes it an excellent substitute of glass substrate in a variety of optical and optoelectronics applications such as flat panel displays, antireflection coatings, solar cells and heat mirrors (DeRudder 2000). Polycarbonate is also highly sensitive to ion irradiation, and is often employed as a resist for electron beam and ion beam lithography and is thus well suited to serve as packaging material for medical disposables which are slated to be radiation sterilized.

2. Experimental

Polycarbonate samples of area 2×2 cm^2 were cut from its 250 μm thick, commercially available and optically transparent sheet. Samples were implanted with 75 KeV Cu$^-$ ions to various doses ranging from 6.4×10^{15} to 1.6×10^{17} ions/cm^2 at a beam current density of ~ 800 nA/cm^2 under a vacuum of ~ 10^{-7} Torr using low energy ion beam facility at Inter University Accelerator Centre (IUAC), New Delhi. The optical absorption and transmission measurements of all the specimens were performed using a Shimadzu double beam double monochromator spectrophotometer (UV-2550) equipped with an integrating sphere assembly ISR-240A in the wavelength range of 190–900 nm with a resolution of 0·5 nm. All these absorption spectra were recorded keeping air as the reference.

The size of the copper nanoparticles embedded in polycarbonate was determined by transmission electron microscopy (TEM) using Technai G20-Stwin Trwas electron microscope operating at 200 kV at Indian Institute of Technology, New Delhi. The current–voltage (I–V) characteristics of the formed nanocomposite were measured using Keithley (6517A) Electrometer at room temperature. The samples were laid between the two electrodes and a testing voltage of 10 V was applied.

3. Results and discussions

The optical absorption spectra of the pristine and 75 KeV Cu$^-$ ion-implanted polycarbonate samples with various doses are shown in the figure 1. Absorption peaks in UV region are due to electronic transitions between occupied and unoccupied molecular orbitals and the spectrum in

this region is particularly sensitive to conjugated bonds. The strongest peaks in the UV are generally due to π–π* transitions which are likely to be associated with the phenyl groups in polycarbonate (Pavia *et al* 1994). The π–π* peak is known to shift to higher wavelengths as conjugation is increased. The absorption spectra of the virgin polycarbonate (curve a, figure 1) show minimum absorption. As a result of copper ion implantation to a dose of 6.4×10^{15} ions/cm^2 (curve b, figure 1) the absorption increases. With a further increase in dose to 1.2×10^{16} ions/cm^2 the absorption continues to increase (curve c, figure 1). At a dose of 1.6×10^{17} ions/cm^2 (curve d, figure 1) along with the increase in absorption, PPR peak, characteristic of copper nanoparticles, centred at 603 nm is also observed (Umeda *et al* 2003; Yuguang *et al* 2005). The presence of the PPR peak is a good indicator of the formation of copper nanoparticles inside the polycarbonate matrix.

The origin of the resonance is attributed to the coupling between the oscillation of the conduction band electrons cloud on the surface of the copper nanoparticles and the incident electromagnetic wave in the quasistatic regime (Kreibig and Vollmer 1995). For particles of diameter less than $\lambda/20$, the optical absorption coefficient α of the composite is given by (Kreibig and Vollmer 1995):

$$\alpha(\text{cm}^{-1}) = (18\pi V n^3 \varepsilon_2)/(\lambda(\varepsilon_1 + 2n^2)^2 + \varepsilon_2^2), \qquad (1)$$

where α is the absorption coefficient of a material of refractive index n embedded with metal spheres of volume fraction V, with radii small compared to the wavelength λ of the incident light. ε_1 and ε_2 are the frequency-dependent real and imaginary components of the metal particle, calculated from the optical constants of their bulk metal
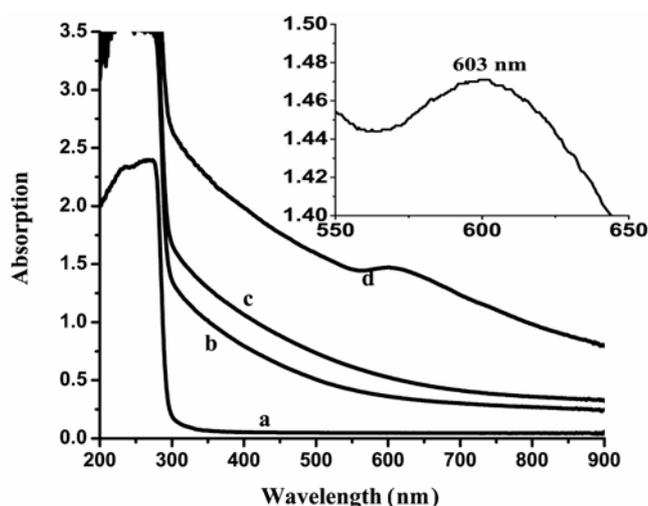
Figure 1. UV-Visible absorption spectra of polycarbonate (a) unimplanted and implanted with 75 KeV to a dose of (b) 6.4×10^{15} Cu$^-$/cm^2, (c) 1.2×10^{16} Cu$^-$/cm^2 and (d) 1.6×10^{17} Cu$^-$/cm^2. (Inset: absorption spectra from 550 to 650 nm of polycarbonate implanted to a dose of 1.6×10^{17} Cu$^-$/cm^2.)

(Palik 1985). The absorption coefficient has its maximum value when $(\varepsilon_1 + 2n^2 = 0)$, which is the condition for the PPR. Thus PPR frequency depends on the dielectric function as well as the metal particle size and composition.

The sizes of copper nanoparticles are calculated according to the following formula, assuming the free particle behaviour of the conduction electrons (Arnold 1975):

$$d = 2hv_f / \Delta E_{1/2}, \qquad (2)$$

where d is the diameter of the copper nanoparticles, v_f ($1 \cdot 57 \times 10^6$ m/s) is the Fermi velocity of electrons in bulk copper, h is Planck's constant, and $\Delta E_{1/2}$ is the FWHM of the absorption band. The above equation is valid as long as the copper nanoparticles dimension is smaller than the mean free path of the electrons in the bulk metal. The mean free path of electrons is about 40 nm at room temperature for bulk copper. Using (2), size of copper nanoparticles comes out to be $\sim 3 \cdot 06$ nm.

The growth of copper nanoparticles in the sample implanted with $1 \cdot 6 \times 10^{17}$ ions/cm^2 was further investigated by TEM. Figure 2(a) shows the TEM micrograph of the
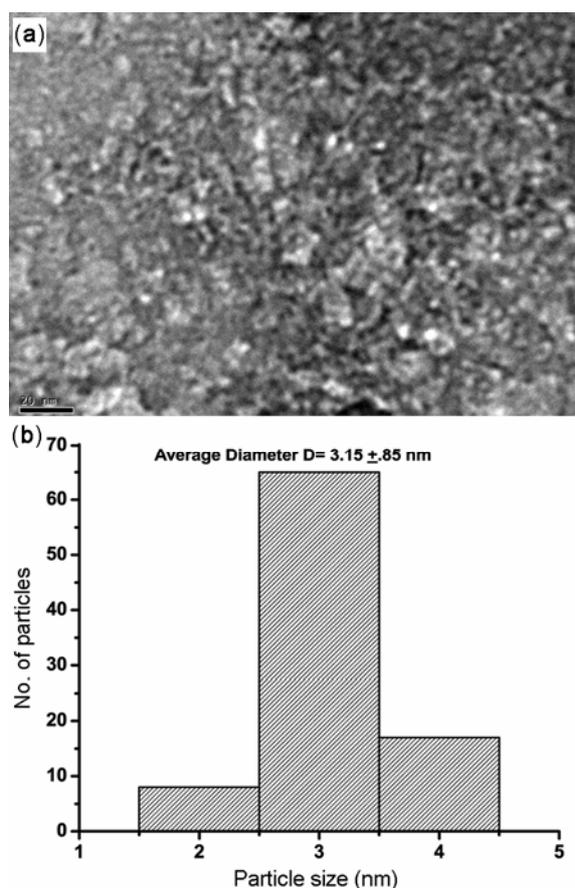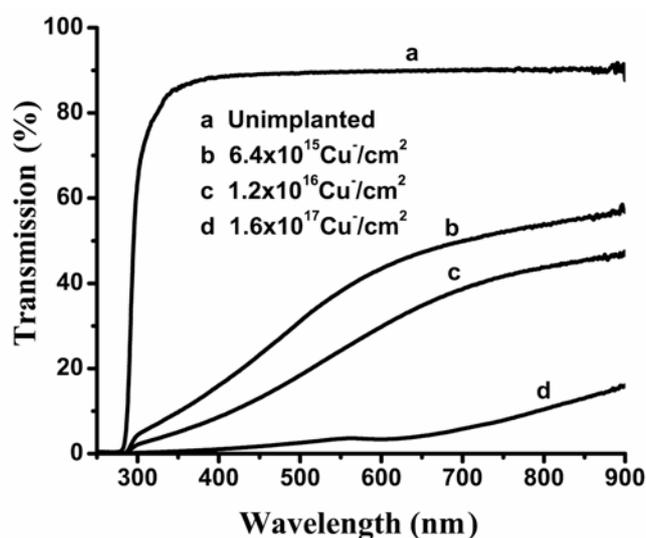
sample implanted with $1 \cdot 6 \times 10^{17}$ ions/cm^2. The size distribution of these copper nanoparticles has been presented in figure 2(b). The average size of the nanoparticles comes out to be $3 \cdot 15 \pm 0 \cdot 85$ nm, which agrees well with the size calculated using UV-Visible spectroscopy.

The transmission spectra of the unimplanted and Cu$^-$ implanted polycarbonate is shown in figure 3. For virgin polycarbonate (curve a, figure 3) transmission is $\sim 90\%$ in the entire visible region and falls sharply thereafter becoming opaque in the UV region. After Cu$^-$ ion implantation to a dose of $6 \cdot 4 \times 10^{15}$ ions/cm^2 (curve b, figure 3) it falls to 60% at 900 nm and then decreases continuously up to 4% at 300 nm. With further increase in ion dose to $1 \cdot 2 \times 10^{16}$ ions/cm^2 (curve c, figure 3) transmission falls to 45% at 900 nm and then decreases continuously up to $\sim 2\%$ at 300 nm. Transmission falls abruptly and reaches in the range of 0–4% in the visible region at a highest implantation dose of $1 \cdot 6 \times 10^{17}$ ions/cm^2 (curve d, figure 3).

The continuous decrease of transmission with increase in ion dose as discussed above can be correlated with the sharp change in colour of the implanted polycarbonate specimens from transparent (virgin) to brown at a dose of $6 \cdot 4 \times 10^{15}$ ions/cm^2 and finally dark brown at a highest implantation dose of $1 \cdot 2 \times 10^{17}$ ions/cm^2. The change in colour can be due to dehydrogenation or formation of colour-sensitive conjugated bonds with loosely bound π-electrons which can easily be excited by the visible photons leading to observed change in colour of the implanted surface (Pavia *et al* 1994).

In the present case of implantation by Cu$^-$ ions at relatively low energy 75 KeV, nuclear collisions prevail in ion–insulator interactions. They displace atoms in the polymer matrix and break some of chemical bonds in it.
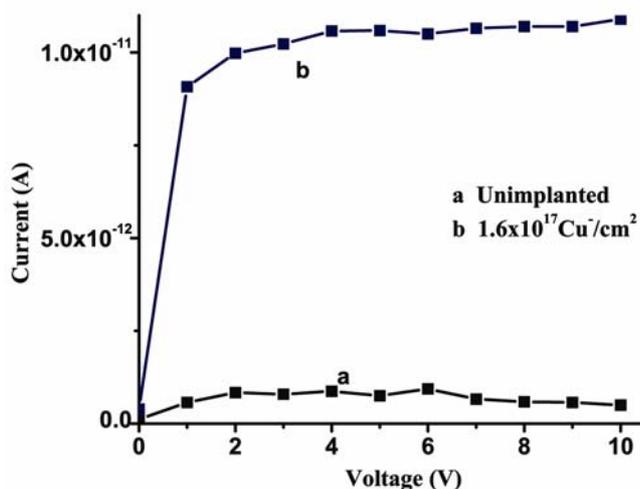

Figure 2. (**a**) TEM micrograph of the copper-polycarbonate nanocomposite synthesized at an implantation dose of $1 \cdot 6 \times 10^{17}$ Cu$^-$/cm^2. (**b**) Size distribution of copper nanoparticles obtained from figure 2(a).

Figure 3. The UV-Visible transmission spectra of the polycarbonate (a) unimplanted and implanted with 75 KeV to a dose of (b) $6 \cdot 4 \times 10^{15}$ Cu$^-$/cm^2, (c) $1 \cdot 2 \times 10^{16}$ Cu$^-$/cm^2 and (d) $1 \cdot 6 \times 10^{17}$ Cu$^-$/cm^2.

In principle, copper atoms may combine with arising organic radical and polymer ions or take part in the oxidation reactions. However, because of a great difference in Gibbs free energy between copper atoms and atoms of polycarbonate elements, Cu–Cu bonding is energetically favourable. The formation of metal nanoparticles proceeds in several stages: the accumulation and subsequent supersaturation of copper atoms in a local surface region of the polymer, the formation of nuclei consisting of several atoms and the growth of copper particles from such nuclei assuming that the nanoparticles nucleate and grow via the successive attachment of copper atoms. Thus it can be concluded that this process is simultaneously governed by the diffusion coefficient and local concentration of copper atoms (Umeda *et al* 2003; Yuguang *et al* 2005).

From figures 1 and 3 it is clear that as a result of Cu^- ion implantation the absorption increases and the absorption edge shifts to longer wavelengths; the shifting of the onset of absorption to longer wavelength has been interpreted as an indicator of the formation of carbonaceous clusters or networks of conjugated unsaturated bonds (Zhu *et al* 2002). During implantation, hydrogen, low molecular hydrocarbons, CO, CO_2 and other gases are released from polymeric materials, which cause the enrichment of carbon atoms leading to the formation of hydrogenated amorphous carbon (Zhu *et al* 2002; Stepanov 2004; Takeda *et al* 2004; Srivastava *et al* 2008).

Thus the implantation of copper not only generates radiation-induced defects but also causes the nucleation and growth of metal nanoparticles. As a result, along with absorption intensity variation, an absorption band associated with copper nanoparticles is also observed.

Figure 4 shows the current–voltage plots of synthesized copper-polycarbonate nanocomposite at the implantation dose of 1.6×10^{17} Cu^-/cm^2 along with unimplanted polycarbonate. It can be discerned from figure 4 that

unimplanted polycarbonate behaves as a perfect insulator, with the embedding of copper nanoparticles of size ~ 3 nm in polymer matrix the resistance of the resulting composite decreases. The electrical properties of nanocomposite films depend upon their microstructure and are strongly linked to the particles nanostructure, particularly to the distance between the particles (Bloor *et al* 2005). The resistance of copper-polycarbonate nanocomposite synthesized at the dose of 1.6×10^{17} Cu^-/cm^2 decreases, because at such a high dose the separation between the nanoparticles is reduced. With smaller distance between nanoparticles, the electrical field induced is large enough to cause the electrons to tunnel from one nanoparticle to a neighbouring one. Consequently conduction occurs via field-induced tunneling and results in the decrease in resistance. The understanding of the electrical behaviour of such nanocomposites can be used to prepare sensors or other devices with a well-defined conductivity.

4. Conclusions

Thus, negative ion implantation is a powerful method of fabrication of copper nanoparticles in polycarbonate matrix. When low energy Cu^- ions are implanted into polycarbonate matrix, besides the increase in absorption intensity with increased dose, an absorption band, characteristic of copper nanoparticles is observed around 603 nm at the dose of 1.6×10^{17} ions/cm^2. This indicates the formation of copper nanoparticles in polycarbonate matrix. TEM further confirms the formation of copper nanoparticles of size 3·15 nm. The I–V characteristics of copper-polycarbonate composites indicate that resistance decreases with increasing copper concentration.

Figure 4. The *I–V* characteristics of (a) unimplanted polycarbonate and (b) copper–polycarbonate nanocomposite synthesized at an implantation dose of 1.6×10^{17} Cu^-/cm^2.

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