Optical properties of surface modified polypropylene by plasma immersion ion implantation technique

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The optical band gap and activation energy of polypropylene (PP) induced by an Ar plasma immersion ion implantation technique were studied in detail. It was revealed that the structural alternation with an increase in polymer chain cross-linking in the ion beam affected layer enhanced the optical properties of PP. The optical band gap, calculated from the transmittance spectra, decreased from 3.44 to 2.85 eV with the Ar plasma ion energy from 10 to 50 keV. The activation energy, determined from the band tail of the transmittance spectra, decreased while the electrical conductivity increased with the Ar plasma ion energy. © *2010 American Institute of Physics.* [doi:10.1063/1.3481417]

Polypropylene (PP) is one of the most widely used polymer in medical, electrical, optical, thermal, and many other applications, due to its low cost, desirable mechanical properties, versatile electronic properties, easiness of processing, and the absence of toxic byproducts.[1–3] Surface treatment of PP with electrons, protons, and plasma irradiation has been reported to affect the structural, optical, electrical as well as the chemical properties, i.e., wettability and biocompatibility for implants.[3–5] Especially optical properties of PP has been studied to explore the decrease in band gap or activation energy for the application on band gap engineering and electronics[4–6] since PP is known to have the higher band gap value ranging from 5.8 to 4.6 eV.[5] Interest on the decreasing the band gap and improvement of conductivity has been focused on the Ar plasma among different plasmas due to its inert characteristic against the organic surface. However, the complex phenomena of the radiation cross-linking and degradation processes occur simultaneously, in most cases, during ion beam irradiation. Therefore, the proper estimation of the optical properties of PP is necessary for further application of PP associated with irradiation using high energy Ar plasma.

This work reports the change in the optical properties of PP with increasing Ar plasma energy. The alternation of the chemical bonds caused by plasma irradiation was explored by chemical analysis, which revealed that chain cross-linking in PP increased with plasma energy. The decrease in the optical band gap and activation energy of PP as well as the increase in the electrical conductivity was explained in terms of the changes in chemical composition induced by the Ar plasma ion implantation.

Ar plasma ion implantation on PP (LG Chem) was carried out using the plasma immersion ion implantation (PIII) technique. The sample coupons with dimensions of 10 mm $\times 10$ mm $\times 2$ mm were placed on the sample stage in the PIII chamber, and the chamber was evacuated to a base pressure of 6×10^{-6} mbar and filled with Ar gas at a pressure of 1.3×10^{-3} mbar, and an rf power of 200 W was applied to the internal antenna to generate inductively coupled plasma. The Ar ion dose was measured to be 5×10^{15} ions/cm^2 from the oscilloscopic trace of the implantation ion current. A target bias voltage of negative 10 to 50 keV was used for implantation.

The thickness of the newly formed stiff layer induced by Ar ion was measured from cross-sectional images with scanning electron microscopy (SEM) (NanoSEM). The ion induced chemical change in PP analyzed by Fourier transform infrared spectroscopy (FT-IR) (Infinity Gold FT-IR), Raman spectroscopy (HORIBA Jobin-Yvon), and x-ray photoelectron spectroscopy (XPS) (PHI 5800). The ultraviolet-visible (UV-Vis) spectrophotometric measurements of the Ar ion implanted PP were performed using a spectrophotometer (Cary 5000) at room temperature. The spectra were recorded by taking a PP sample as reference and hence transmission due to the Ar ion implanted PP layer only was obtained. The electrical property was measured in a focused ion beam system (Quanta 3D) by a nanomanipulator (Kleindiek with Agilent P15008 multimeter) including a two point probe system.

Transport of ions in matter (TRIM) simulation has been performed for the calculation of the thickness of the Ar ion implanted PP layer. The energies of Ar ions were varied from 10 to 50 keV and the mass of Ar ion was treated 39.962 atomic mass unit and total 9999 Ar ions are implanted onto the polymer surface.

The cross-section of the ion implanted surface clearly revealed the stiff layer with a uniform thickness of about 75 nm formed by Ar ion implantation as shown in Fig. 1(a). The thickness of the ion implanted layer was measured to increase from 35 to 102 nm with increasing Ar plasma ion energy from 10 to 50 keV, which showed similarity to the value calculated using TRIM simulation from 28 to 87 nm as shown in Fig. 1(b).

In Fig. 2(a) the FT-IR spectra shows different CH$_3$ and CH$_2$ bonds which represents the characteristic of PP.[3,7,9] The

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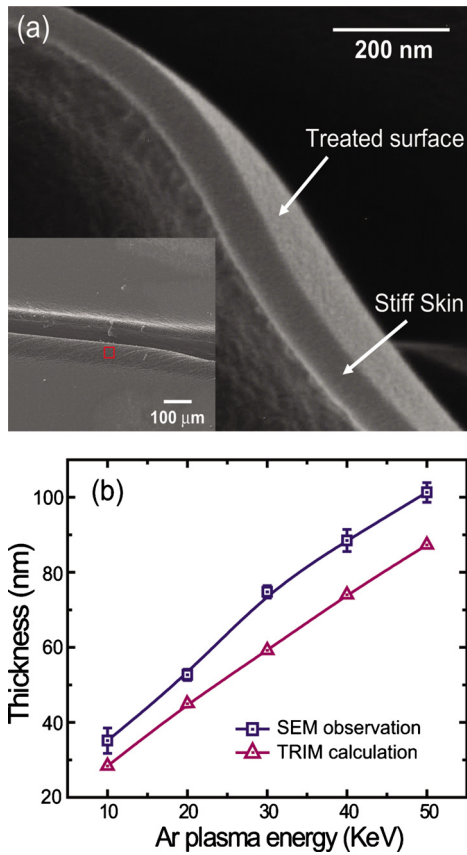
FIG. 1. (Color online) (a) A cross sectional SEM image taken from the square box of the scratch track of the Ar ion implanted PP at 30 keV and an inset of a SEM image showed a PP surface scratched with a diamond tip for the observation of cross-section and (b) variation in the Ar ion implanted layer thickness with the plasma energy estimated with experimental observation and TRIM simulation.

inset of Fig. 2(a) showed the peaks at 2950 and 2870–2880 cm^{-1} were assigned to the CH$_3$ asymmetric and symmetric stretching modes, respectively, and the peaks at 2920 and 2836 cm^{-1} were assigned to the CH$_2$ asymmetric stretching vibration modes. Clearly, from Fig. 2(b), the Ar plasma ion implantation decreased the amount of CH$_3$ groups in the PP and transformed them into CH$_2$ groups inducing cross-linking in the PP. The plasma treatment of polymer surface using Ar ion would break C–C bonds, leading to the production of carbon radicals. The Ar ion induced the radicals on PP surface and these radicals reacted with each other to form cross-linked layers.[3,8]

In Fig. 2(c) the Raman peaks at 810, 842, and 1330 cm^{-1}, assigned to the CH$_2$ rocking, C–C stretching and CH bending, and CH$_2$ twisting modes,[9,10] decreased in intensity with plasma energy. The Raman analysis showed that amorphous carbon formed in the ion implanted PP, as an sp^2 and sp^3 hybridized mixture.

XPS analysis shows that the untreated PP film contains 6.1% C–O groups and 93.9% C–C or C–H groups. After 50 keV Ar ion irradiation, the concentration of the C–O groups increases to 16.1% while the concentration of the C–C or C–H groups decreases to approximately 75.3% in Fig. 2(d). Through the depth of the Ar ion implanted PP films, it is clear that the C content on the surface decreased as PP samples irradiated by Ar ion plasma while the O content increased.

Using the transmittance data, the optical band gap energy (E_g) of PP was obtained from Tauc expression[11] given below

$$\alpha h\nu = A(h\nu - E_g)^{1/2}, \tag{1}$$

where A is a constant and $h\nu$ is the incident photon energy. The optical band gap was calculated from the $(\alpha h\nu)^2$ versus
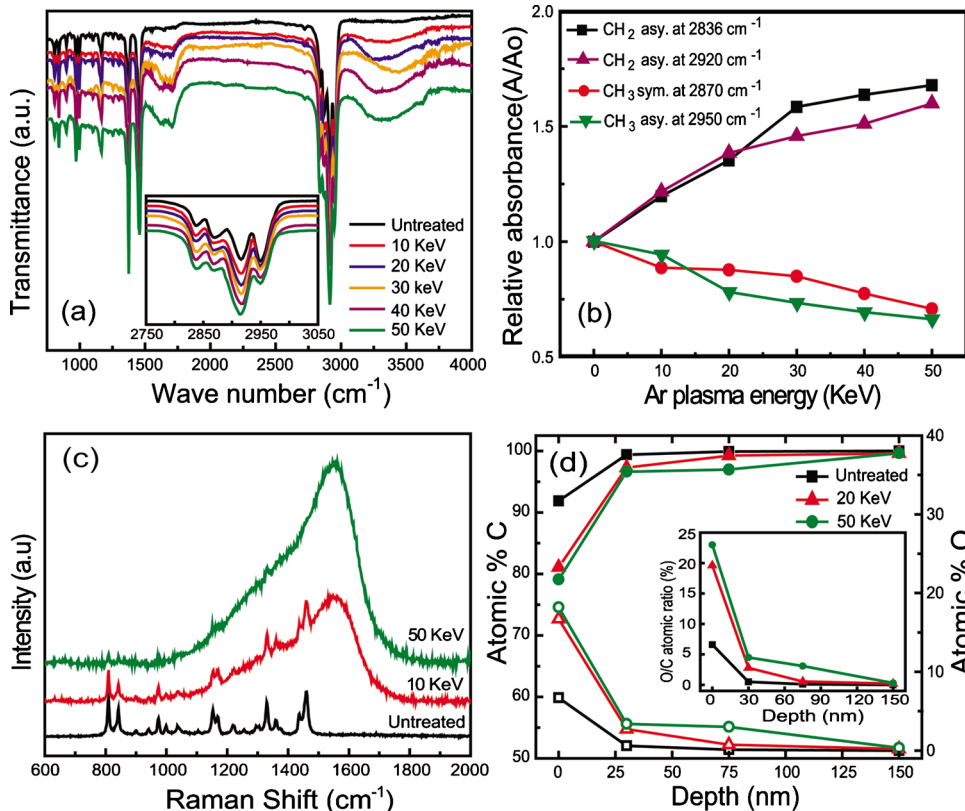

FIG. 2. (Color online) (a) FT-IR spectra of the untreated and Ar ion implanted PP and the insets corresponding magnified FT-IR spectra in the range of 2750–3050 cm^{-1} (b) variation in the relative absorbance (A/A$_0$, where A$_0$ and A are the absorbance of the untreated and Ar ion implanted PP, respectively) of different CH$_n$(n $=2,3$) groups with the Ar plasma ion energy. (c) Raman spectra of the untreated and Ar ion implanted PP and (d) XPS depth profile of the untreated and Ar ion implanted PP (open symbols for atomic percent of O and solid symbols for atomic percent of C and the change in O/C atomic ratio with depth in an inset.
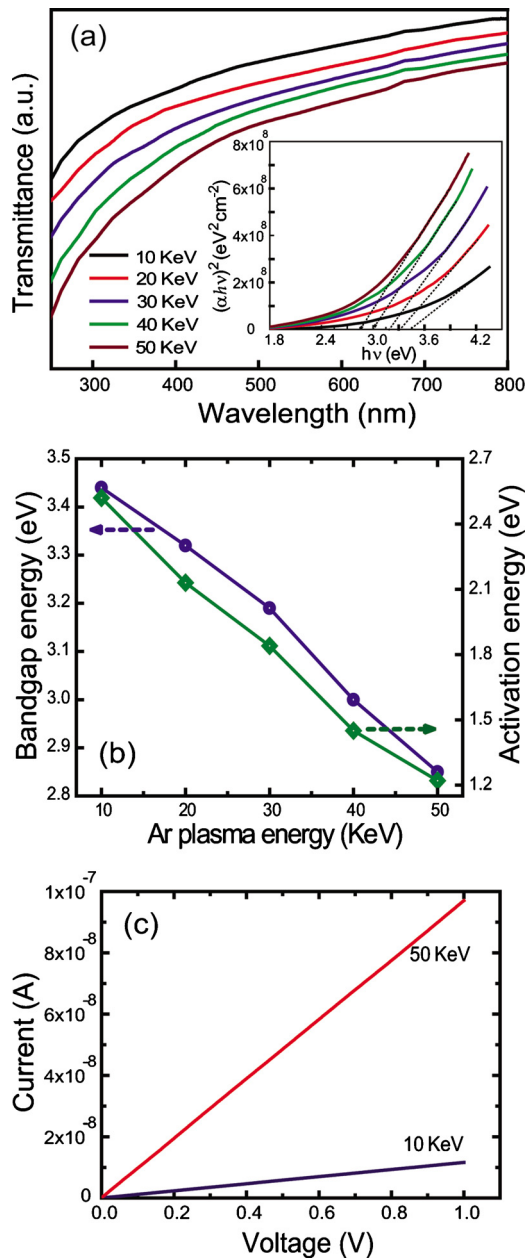
FIG. 3. (Color online) (a) Transmittance spectra of the Ar ion implanted PP and an inset Tauc plot to determine the optical band gap, (b) variation in the optical band gap and the activation energy with the Ar plasma ion energy and (c) room temperature I–V curves of the Ar ion implanted PP.

$h\nu$ plot [an inset of Fig. 3(a)] to the $h\nu$ axis at $\alpha=0$. Figure 3(b) shows that the optical band gap of the PP decreased from 3.44 to 2.85 eV for different Ar plasma energies ranging from 10 to 50 keV. The Ar plasma ion implantation increased the formation of carbon–carbon double bonds (as confirmed by Raman analysis), which promoted the delocalization of charge carriers. As a result, the band gap and the activation energy decreased. Therefore, conjugation and carbonization seemed to be main process responsible for the decrease in the band gap of PP irradiated by Ar plasma.[12] This decrease in the optical band gap may also be attributed to the creation of point defects during the plasma ion implantation caused by the interaction of ions or secondary electrons with the lattice atoms and by inelastic multiple collisions.[13,14]

The urbach energy is one of the standard measurements of the inhomogeneous disorder in semiconducting materials.[15] The activation energy was calculated from the band tail using the Urbach rule given by Eq. (2)

$$\alpha = B\,\exp(h\nu/E_a),\tag{2}$$

where B is a constant and E_a the activation energy. Figure 3(b) indicates that as the Ar plasma energy increased from 10 to 50 eV, the activation energy gradually decreased by 2.52 to 1.22 eV. The decrease in the E_a of PP might be associated with formation of clusters of amorphous carbon within the Ar ion implanted PP as confirmed by Raman measurement. The clusters of amorphous carbon and the point defects bring a higher carrier concentration on band structure.[16] Presence of these defects might lead to the formation of lower-energy states and decrease the gap between the conduction and valence bands in irradiated polymer. Consequently, the activation energy of the PP decreased with increasing Ar plasma ion energy. Correspondingly the conductivity of the Ar plasma ion implanted PP was measured to increase from 4.6×10^{-6} to 3.9×10^{-5} Ω cm^{-1} as the plasma energy increased from 10 to 50 keV in Fig. 3(c), which is comparable with the range of the chemically modified grafted PP.[17]

In summary, the optical properties of PP were examined after Ar plasma ion implantation with energies from 10 to 50 keV. The optical band gap decreased as well as the electrical conductivity increased with Ar plasma energy due to the structural evolution of carbon–carbon double bond formation. The observation of the optical and electrical properties could be profitably used in tailoring the properties of this semiconductor material.

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