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Iodine doping in amorphous carbon thin-films for optoelectronic devices

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Abstract

We report the effects of iodine doping on the optical and structural properties of amorphous carbon thin-films grown on silicon and quartz substrates by microwave surface wave plasma chemical vapor deposition (CVD) at low temperature (<100 °C). For film deposition, we used Ar and CH₄ as plasma source gases. The films were characterized by UV/Vis/NIR spectroscopy, X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy measurements. The optical band gap of the films decreased from 3 to 0.8 eV corresponding to non-doping to iodine doping conditions. The XPS results confirm the successful doping of iodine in the films. The Raman results show that iodine doping induced more graphitization in the films.

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1. Introduction

Carbon (C) is a remarkable element exists in different forms ranging from insulator diamond to metallic graphite to conducting/semiconducting nanotubes [1]. In recent research, amorphous carbon (a-C) has been shown to behave as a semiconducting material, which is able to accept dopants, shows photoconductivity and suitable for optoelectronic devices [2]. However, there are some problems such as high density of defects due to the sp²/ sp³ bonding structure and the difficulties in controlling the conduction type, carrier concentration and optical band gap [3].

When we attempt to utilize a-C as an alternative material in optoelectronic devices, control of the conduction type of a-C film is indispensable [4]. Effective doping can modify optoelectronic properties of semiconductor materials, in particular optical band gap and photoconductivity. Doping of a-C with n-type (e.g. phosphorus (P) and nitrogen (N_2)) and p-type (e.g. Boron (B)) has been attempted by several researchers [3–7]. However, the doping prospect of a-C remains unclear. A new method of doping by iodine (I) called oxidation has been introduced by Shirakawa et al. [8] for hydrocarbon polyacetylene $(CH)_x$ [9–11]. This method has also been applied for a-C and diamond-like carbon (DLC) films, and the preliminary results showed improvement on optoelectronic properties [12]. However, the mechanism of doping and the doping induced structural changes were not clear in the earlier study.

In this paper, we report the effects of I-doping on optical and structural properties of a-C thin-films grown on quartz and silicon (Si) substrates by microwave (MW) surface wave plasma (SWP) chemical vapor deposition (CVD) at low temperature (<100 °C).

2. Experimental details

a-C thin-films were deposited on quartz and Si substrates by a 2.45 GHz MW SWP CVD, a newly developed deposition method [12–14]. The substrates were cleaned beforehand by acetone and methanol in an ultrasonic bath and then rinsed by ultra-pure water. The Si substrates were

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etched with diluted hydrofluoric acid (10%) in order to remove the resistive native oxide layer over the surface. The CVD chamber was evacuated to a base pressure at approximately 5×10^{-4} Pa using a turbomolecular pump. For film deposition, we used Ar (280 sccm) as carrier gas and CH₄ (10 sccm) as carbon precursor. The launched microwave power was typically 500 W at a gas composition pressure of 55 Pa in the CVD chamber. The duration of film deposition was 60 min. For I-doping, we employed pyrolysis of the CVD-deposited a-C films to I-vapor for about 10 min. Pyrolysis was carried out using a double furnace set-up, one for heating the source material (I) placed in a quartz boat and the other for controlling the sample temperature at 80 and 200 °C, respectively, using Ar as a carrier gas [12].

The optical properties of the films were investigated by JASCO V-570 UV/VIS/NIR spectrophotometer. The X-rays photoelectron spectroscopy (XPS) was measured by ESCA-3300 KM Electron Spectrometer utilizing an Al K_{α} (hv = 1486.6 eV) radiation as an X-ray source, under high vacuum conditions of about 10^{-7} Pa. The Raman spectra (RS) was obtained at room ambient conditions in the quasi-backscattering geometry using 488 nm line of Ar⁺ laser operating at a power of 200 mW while at the sample it was about 5 mW.

3. Results and discussion

The film (thickness: 460 nm) deposited in this experiment is diamond-like a-C, which promises a good-quality semiconducting thin-film for optoelectronic devices [12].

To study the optical characteristics of a-C films, we carried out the reflectance and transmittance measurements by UV/Vis/NIR spectroscopy in the wavelength range of 200-2000 nm. The optical band gaps were obtained by Tauc equation [15]. As shown in Fig. 1, we found that the absorption coefficient (α) of a-C films increased significantly after I-doping. Interestingly, the optical band gap of the films decreased from 3 to 0.8 eV after I-doping. The results suggest that the I-doping in a-C films induced graphitization and, consequently, decreasing of the optical band gap.

The XPS was used to investigate chemical bonding and structural properties of the films [13]. Although there are still some controversies about the assignments of the individual components of the C 1s and I 3d core level spectra, the XPS analysis is one of the most likely used techniques in the literatures to characterize the chemical bonding structures, and to acquire useful information on the chemical environment around O, C and I of a-C phases as shown in Fig. 2. In order to confirm the homogenous distribution of I in the film, the XPS data has been taken as an average from different positions of the sample. As shown in Fig. 3, the XPS result reveals a clear difference between undoped and I-doped a-C films. The I-doped a-C film contains I at atomic concentration of 0.26% and mass concentration of 2.66%.



Fig. 1. Optical absorption edge of the a-C films before and after I-doping.



Fig. 2. XPS (hv = 1486.6 eV) wide scans of a-C films before and after I-doping.



Fig. 3. XPS (hv = 1486.6 eV) I 3d core-level spectrum of I-doped a-C film compared with the spectrum of undoped film.

Raman spectroscopy is a very popular, non-destructive tool for investigating the structural characteristics of a-C and DLC films [16-18]. RS provides a wide range of structural and phase disorder information. RS of two crystalline forms of C; graphite and diamond are well known [19–22]. The first order RS consist of a single line at 1332 cm^{-1} for diamond [23], and 1580 cm^{-1} for single crystal graphite [20,24]. The latter, known as graphite peak (G peak), results from the Raman allowed E_{2g} mode [25], while another line appears also at 1355 cm⁻¹ for polycrystalline graphite, known as disorder peak (D peak) results from the breakdown of the k-vector conservation rule of the disordered lattice [26] and grain boundary effect [20]. Generally, the G and D peaks are the most used lines in RS to characterize the C films. The D peak represents disordered sp²-hybridized C with an amount of sp³hybridized C, while the G peak represents graphite-like sp²-hybridized C in the films [27,28]. Fig. 4 shows the RS of the films before and after I-doping in the range of $1000-1800 \text{ cm}^{-1}$. The RS of the undoped film revealed its amorphous nature. It is clear that the board band of the film splitted into D and G peaks after I-doping due to the graphitization, as can also be seen from the optical properties of the films (Fig. 1). In order to evaluate the structural features, the experimental data were best fitted (accuracy factor ~ 0.95) by two peaks, considering Gaussian line shapes and linear background, and a typical plot of this kind is shown in Fig. 5 for the I-doped film. The peak position, the peak full-width at half-maximum



Fig. 4. RS of the a-C films before and after I-doping.



Fig. 5. Gaussian fitting for RS of I-doped a-C film.

(FWHM) and the integrated intensity ratio of the two peaks (I_D/I_G) are obtained from the Gaussian fittings. For D-peak, the position and FWHM were 1357.62 and 233.11 cm⁻¹, respectively. While for G-peak, the position and FWHM were 1588.96 and 90.07 cm⁻¹, respectively. The I_D/I_G was calculated as 2.35. The Raman results suggest that the film contains a mixture of tetrahedral bonded C (sp³-C bond) and trihedral bonded C (sp²-C bond) bonds, and the latter acts as a localized conduction state [29]. Therefore, the optical band gap is determined by the sp^3/sp^2 -hybridized C ratio.

Finally, the present results suggest that I-doping in a-C films induces graphitization as a result of structural changes due to sp^3/sp^2 carbon bonding network. Consequently, the I-induced graphitization helps to improve optoelectronic properties of a-C films applicable for photovoltaic devices.

4. Conclusions

We investigated the properties of the a-C film before and after I-doping. The optical band gap of the film decreased from 3 to 0.8 eV after I-doping. The XPS analysis confirmed the presence of I-bonded a-C that indicates the successful doping of I in the film. The Raman results showed that the graphitization of film intensified after Idoping. Further research is in progress to optimize the dopants, and to improve quality of the films by reducing the bonding defects.

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