

Rearrangements of sp^2/sp^3 hybridized bonding with phosphorus incorporation in pulsed laser deposited semiconducting carbon films by X-ray photoelectron spectroscopic analysis

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Abstract

The carbon films were grown on p-type silicon substrate at room temperature by pulsed (XeCl) laser deposition technique using camphoric carbon target containing 1%, 3%, 5% and 7% of phosphorus (P) by mass. The analysis of X-ray photoelectron spectroscopy spectra of the C1s region in these films shows the presence of sp^2 and sp^3 hybridized carbon and a sp^2 satellite peak due to $\pi-\pi^*$ shake up. The sp^2 content is seen to remain almost constant with P content. The FWHM of the sp^2 peak increases up to 5% P but decreases for 7% P probably due to clustering of sp^2 chains and this clustering in the sp^2 phase probably decreases the band gap for the 7% P film. With P incorporation, the tetrahedral bonding configurations of the carbon network do not change appreciably, therefore, suggesting the scope of phosphorus as a potential dopant in carbon films.

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1. Introduction

Nowadays, research on carbon thin films has attracted much attention in the field of semiconductor technologies and tribology industries including potential biomedical coatings due to some of its extraordinary optoelectronic and mechanical properties [1] and biocompatibility [2]. Various carbon-based heterostructures on silicon have already been reported [3] and thereby demonstrates the potentiality of carbon materials in electronic devices.

Effective doping can modify electronic properties, especially gap states, conductivity, etc. Attempts have been made to dope carbon films using various elements [4–13]. However, most of the studies are reported to have concentrated on nitrogen (N) as dopant with contradictory results [10–13]. Unfortunately, controlled doping of N in carbon is very difficult because it encourages carbon to form sp^2 bonding and adopt many bonding configurations such as sp^3 and sp^2 non-doping sites along with doping sites in carbon network [1,13]. Phosphorous (P) is the

widely used n-type impurity in silicon [14] and it is expected that P in carbon might be favorable to form a tetrahedral coordinated bonding network [7]. P is already reported to be incorporated in carbon for its applications in electronics [3] and biocompatibility in cardiovascular implants [2]. A small amount of P incorporated in carbon has shown n-type behavior [4]. Using camphor ($C_{10}H_{16}O$), a natural source, as a starting precursor in the pulsed laser deposition (PLD) system, we have reported successful P doping in a relatively smaller gap diamond-like carbon (DLC) film with optical gap close to that of silicon [6], which has a scope in optoelectronic device applications. Our works on P doped carbon for its photovoltaic (PV) applications reveal the performance of carbon films and PV device characteristics obtained from camphor precursor are better compared to those obtained from conventional graphite target [3,15]. A full understanding of the atomic structure of doped carbon is very necessary for its practical applications in electronic devices. Considerable work has been done to understand the atomic structure and bonding configurations of the nitrogenated/nitrogen doped carbon films [10–13]; however, the bonding configurations of P incorporated carbon films remain almost unclear.

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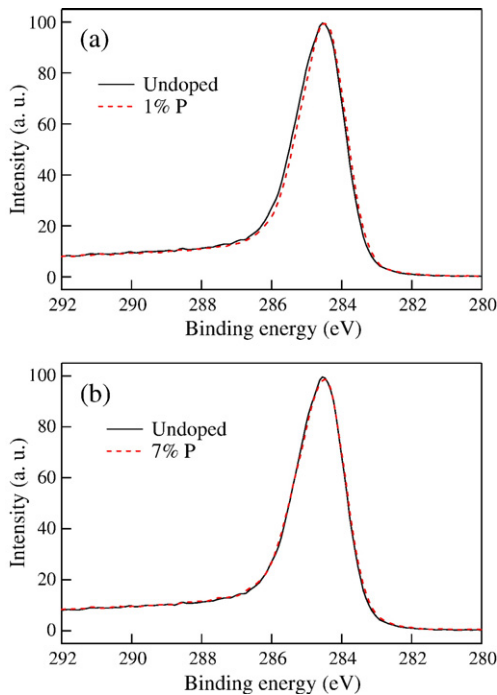


Fig. 1. XPS C1s region of pulsed laser deposited carbon films obtained from camphoric carbon soot targets containing phosphorus (P). (a) Shows the comparison of the XPS spectra of films deposited from 0% P (undoped) and 1% P in CC targets, and (b) shows the comparison of the XPS spectra of the films deposited from 0% P (undoped) and 7% P content in CC targets.

In this work, we have investigated the atomic structure and bonding environments of the pulsed laser deposited P incorporated carbon films obtained from the CC targets. X-ray photoelectron spectroscopy (XPS) measurements of the undoped film as well as films deposited from targets containing 1%, 3%, 5% and 7% P by mass on silicon substrates were done. The findings of the XPS spectra are also correlated with the electron spin resonance (ESR) spectroscopic observations. The rearrangement of carbon trigonal (sp^2) and tetrahedral (sp^3) hybridized bonding configurations upon P incorporation in the PLD grown semiconducting carbon films obtained from the CC target is presented for the first time.

2. Experimental details

Carbon films were deposited on silicon substrates by a XeCl excimer laser. Details of the chemical structure of the starting precursor camphor, the camphor burning system, target preparation and deposition method have been described elsewhere [6]. In order to dope, the CC soot was mixed with varying amounts of red phosphorus powder (1, 3, 5 and 7% by mass) and compressed into pellets. Atomic % of P in the film was determined by XPS analyses. The instrument used was SSX-100 XPS system from Surface Science Instruments utilizing $AlK\alpha$ ($h\nu=1486.6$ eV) radiation, under high vacuum conditions of $\sim 10^{-10}$ Torr.

3. Results and discussions

The XPS measurement was carried out in the range of 0 to 1000 eV, which allowed detection of the elements present. For

quantification, appropriate sensitivity factors of the elements were used. The P content in the film increases from about 0.29 to 2 at.% as the P content increases from 1 to 7% by mass in the target [6]. The measurement of XPS C1s region is carried out separately to study the bonding configuration of carbon and the effect of P incorporation in these films. Etching is also done from the surface to the inside of the film after sputtering up to of 10 min with Ar^+ ions to remove the thin layer of oxidized species present on the surface. For a particular film, from the surface to the inside of the film it is seen that the atomic % of oxygen decreases rapidly initially and becomes almost saturated to a very low level for the sputtering up to 10 min. Therefore, to eliminate the surface oxygen effect, the analysis is done for the C1s regions acquired after the films had been sputtered for 10 min. The XPS C1s spectrum for the undoped film is peaked at about 284.5 eV. The spectrum for the film deposited from 1% P in the CC target shifts slightly towards lower binding energy (Fig. 1(a)). With the increase of the P content, the spectrum shifts towards higher binding energy and the peak position of the film deposited from 7% P in the CC target is almost similar to that of the film deposited from the undoped CC target (Fig. 1(b)). To understand clearly, the XPS C1s region is fitted with three components peaked at about 284.5, 285.5 and 287 eV, which correspond to sp^2 bonded carbon, sp^3 bonded carbon and sp^2 carbon satellite peak [16]. The peak height and positions were allowed to vary to obtain the best fit of the experimental data. The background was removed by using the method proposed by Shirley [17]. Moreover, the combination of 90% Gaussian and 10% Lorentzian peak shape functions is used as deconvolution of the peaks using this Gaussian–Lorentzian sum functions has resulted to the best fit. In addition to the normal peak for C–C (sp^2) at the binding energy of 284.5 eV, we get an extra peak for C–C (sp^2 satellite) at the binding energy of 287 eV due to energy loss during the photoionization processes. A typical plot of the fitted spectra is shown in Fig. 2 for the films deposited from 1% P

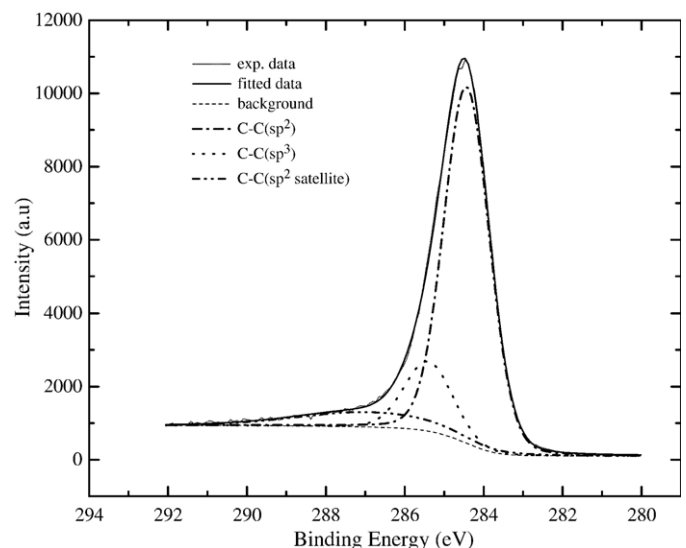


Fig. 2. The fitted curves, sp^3 peak, sp^2 peak, sp^2 satellite peak, together with its Shirley background and measured XPS C1s spectrum of pulsed laser deposited carbon films obtained from camphoric carbon soot targets containing 1% P.

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