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Temperature dependence of the optical gap of diamond-like carbon films investigated by a piezoelectric photothermal spectroscopy

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Abstract

Temperature dependences of the optical gap of diamond-like carbon (DLC) films were investigated by using a piezoelectric photothermal (PPT) spectroscopy, that detects the nonradiative transition of photoexcited electrons. Since the PPT signal intensity is expected to be proportional to its optical absorption coefficient, the optical gap was estimated by a Tauc plot. The temperature coefficient of the optical gap energy was found to be very small compared with that of other semiconductor such as Si. This result implies that the device performance is expected to be stable by temperature change and the DLC films are excellent as the next generation solar cells materials.

Keywords: diamond-like carbon; piezoelectric photothermal spectroscopy; nonradiative transition; temperature coefficient;

1. Introduction

Recently, solar cells have attracted much attention as one of clean energy sources and their market increases year by year. This is because an exhaustion of fossil energy and an environmental pollution become more serious. Especially, silicon solar cells, including crystalline, thin film, amorphous, and microcrystalline forms, occupy more than 90% of the market. However, the conversion efficiency of most

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available solar cells of bulk silicon is too low to become the major power source. Multi-junction solar cell is a most promising candidate technology for extremely high efficiency compared to the traditional solar cells made of a single semiconductor *p-n* junction. Multi-junction solar cells consist of the several *p-n* junctions to absorb a wide wavelength range of the sunlight. In fact, an InGaP/GaAs/Ge 3-junction solar cell showing a high conversion efficiency of 31.7% have been realized [1]. However, the generation of the misfit dislocations that will significantly degrade the conversion efficiency is still inevitable.

Diamond-like carbon (DLC) is an amorphous carbon consisting of an inhomogeneous mixture of the diamond like (sp^3) and graphite like (sp^2) bonds. Since the optical energy gap of DLC varies over a wide range of energy by changing the compositional ratio of sp^3 to sp^2 bonds, single material multi-junction solar cell could be realized [2]. We have investigated the optical properties of DLC films deposited on the Si substrate by using the piezoelectric photothermal (PPT) and surface photovoltage (SPV) spectroscopies. The former detects the nonradiative transition of photoexcited electrons [3] and the latter detects the surface potential change by the carrier accumulation [4]. Since the PPT can be employed to obtain the optical absorption coefficient of highly transparent and thin semiconductor samples, we have clearly demonstrated that optical energy gap of DLC changed by the sp^3 ratio ($= sp^3/(sp^2+sp^3)$) and discussed the photovoltaic performances of DLC films [5]. In this study, we investigate the temperature coefficient of E_{og} of DLC films by using PPT technique. Since the short-circuit current (I_{sc}) and open-circuit voltage (V_{oc}) is drastically influenced by the bandgap energy, the temperature coefficient of optical energy gap is an important parameter for improvement conversion efficiency of solar cells [6].

2. Experimental Procedure

The Si-doped DLC films were deposited on quartz substrates by the plasma-enhanced chemical vapor deposition (PECVD) method using methane (CH_4), argon (Ar), and monomethylsilane [MMS; $SiH_3(CH_3)$] gasses [7]. The deposition of DLC films was carried out under a pressure of 0.3 Pa and a negative bias voltage was changed from -100 to -1000 V for different film deposition. An Ar flow rate was 22 sccm, whereas CH_4 and MMS flow rates were changed but keeping up the total flow rate of 44 sccm. The substrate temperature during the deposition was kept lower than 75 °C. The thickness of the DLC films were 300 nm estimated by the observed interference fringes by the Fourier transform infrared spectroscopy.

The chemical bonding of the deposited films was characterized by X-ray photoelectron spectroscopy (XPS). Obtained emission spectra from C 1s orbital in DLC films were decomposed into two components by using a Voigt function that consists of the convolution of the Lorentzian and the Gaussian profile functions. The sp^3 ratios of DLC films were estimated by using the integrated intensities of two components, one is the sp^3 hybrids with binding energy of 285.2 eV and other is the sp^2 hybrids with binding energy of 284.3 eV [8]. In this study, five DLC films with sp^3 ratios, 29, 39, 44, 50, and 55% were prepared.

For the PPT measurements, a disk-shaped PZT detector was directly attached to the DLC film surface of the sample by using conductive paste. The sample was then mounted on the cold finger of a liquid-nitrogen cryostat. A 300 W halogen lamp attached to a grating monochromator was used as the probing light. The temperature of the sample was changed in the dark. After having confirmed that the temperature of the sample became sufficiently stable, the probing light was illuminated from the quartz substrate side and heat generated by the nonradiative transition was detected as the PPT signal. Obtained spectrum was then corrected with the wavelength and temperature dependences of the experimental apparatus.

3. Results and Discussion

Figure 1 shows the PPT spectra of DLC films with different sp^3 ratios at room temperature. The PPT signal intensity of sp^3 = 29% sample increased with increasing photon energy from around 1.0 eV. The signals of other sp^3 ratio samples also increased with increasing photon energy, whereas the signal intensities are very low. For sp^3 = 29% sample, the optical interference fringes within the DLC film appears in the spectrum as shown in the figure. We have already reported to calibrate this effect in the PPT spectrum of microcrystalline silicon [9, 10]. Therefore, we could subtract the fringes for discussing the band edge energy.

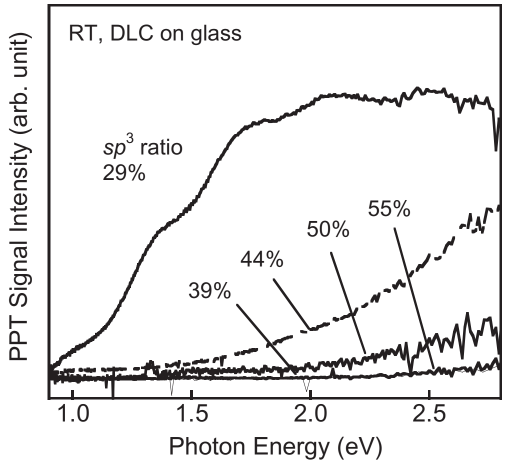

Fig. 1. The PPT spectra of DLC films with different sp^3 ratios at room temperature

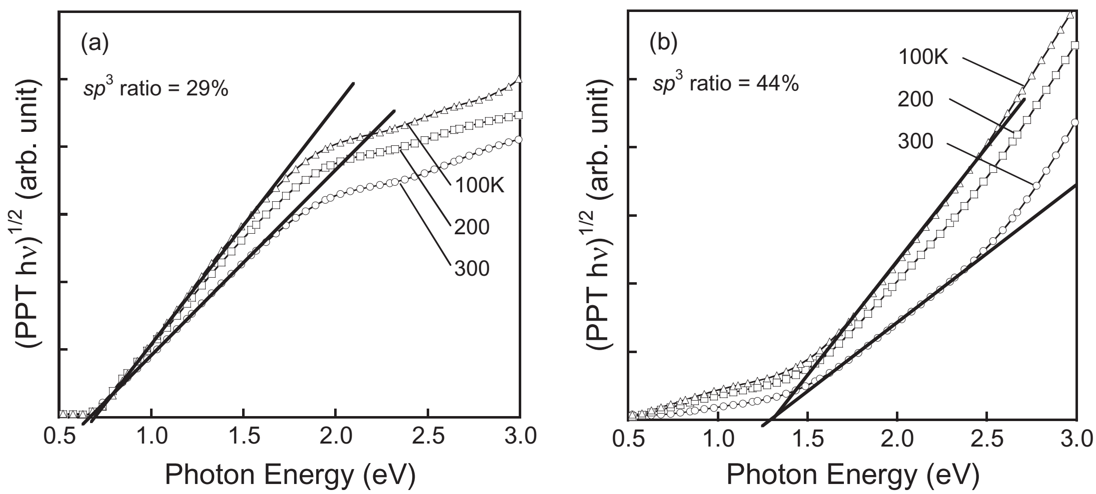

Fig. 2. $(\mathrm{PPT}\ h\nu)^{1/2}$ plots as a function of hν for sp^3 ratios of (a) 29 and (b) 44% samples

To determine the optical gap, we employed a Tauc plot that is often used to characterize practical optical gap of amorphous materials [11]. A Tauc plot is defined as an expression of $(\alpha\ h\nu)^{1/2} = C^*(h\nu - E_{og})$, where α is an optical absorption coefficient, hν the photon energy, E_{og} the effective optical gap, and C is a constant. In the case of thin or transparent samples of DLC films as in the present study, the PPT signal intensity is expected to be proportional to its α [3]. Therefore, we plotted the (PPT hν)$^{1/2}$ as a function of hν in place of (α hν)$^{1/2}$. The results for sp^3 = 29 and 44% samples are shown in Figs. 2(a) and 2(b), respectively. The E_{og} of DLC film was estimated from the extrapolation of the straight lines to (PPT hν)$^{1/2}$ = 0, as shown in the figures.

In Fig. 2(a), we estimated values of E_{og} of sp^3 = 29% sample at 100 and 300 K to be 0.68 and 0.65 eV, respectively. The change of E_{og} by increasing the temperature was small. For sp^3 = 44% sample, as shown in Fig. 2(b), signal tailing was observed in the PPT spectra below around the optical gap of 1.5 eV for all the measured temperatures. As discussed in the reference [2], DLC is considered to be an amorphous carbon consisting of an inhomogeneous mixture of the sp^3 and sp^2 bonding phases. Considering the local band gap as a function of distance in this amorphous structure, the sp^3 bonding phase has a wider gap, between the σ and σ* states, whereas sp^2 bonding phase has a smaller gap, which varies strongly depending on the width of the π and π* states [2]. In this situation, sp^3 matrix acts as a tunnel barrier between each sp^2 cluster. The E_{og} of a DLC film is, then, given by the average band gap of the clusters in it. The range of sp^2 cluster sizes will give rise to a broad absorption tail, not a sharp band gap. We then concluded that the PPT signal tails below 1.5 eV observed in Fig. 2(b) were also band to band transition within sp^2. We then estimated values of E_{og} of sp^3 = 44% sample at 100 and 300 K to be approximately 1.32 and 1.31 eV, respectively. The decrease of value of E_{og} by increasing the temperature was small, too.

Figure 3 shows a temperature change of values of E_{og} of sp^3 = 29 and 44% samples from the (PPT hν)$^{1/2}$ plots. The temperature coefficients (dE_{og}/dT) were estimated to be -1.50 and -0.65 × 10^{-4} eV/K, respectively. The values of dE_{og}/dT tended to decrease with increasing sp^3 ratio. The small value of dE_{og}/dT =-0.54 × 10^{-4} eV/K for diamond (sp^3 = 100%) [12] may also account for the present results.

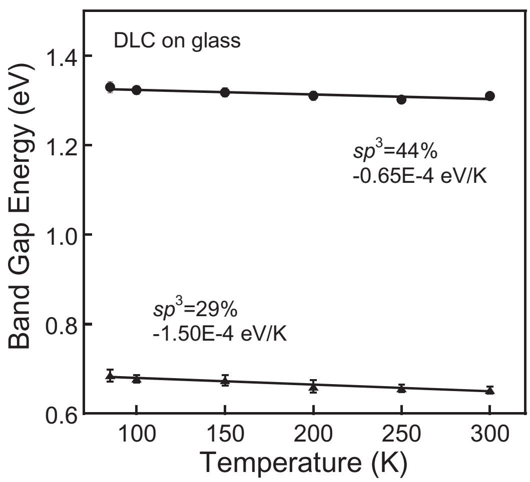

Fig. 3. Temperature dependences of band gap energies of DLC films of sp^3 = 29 and 44% samples

We then discuss the potential of DLC films as the solar cell materials. It was found that obtained values of dE_{og}/dT of DLC films were very small comparing with that of other semiconductors, such as Si (-4.73) and GaAs (-5.41 × 10^{-4} eV/K) [13]. A realistic operating temperature of the solar cells is approximately 80 degrees Celsius. If the band gap decreased by increasing the operating temperature of the solar cells, V_{oc} decreases and I_{sc} increases at the same time [6]. Because the conversion efficiency of solar cells (η) is proportional to V_{oc} × I_{sc} × fill factor (FF), dE_{og}/dT is an important parameter for improvement conversion efficiency of solar cells. Small value of dE_{og}/dT is required. Since the DLC films showed a variability of E_{og} by sp^3 ratio [5] and a very small value of dE_{og}/dT, we can make a single material multi-junction solar cells without degradation by the operating temperature. In addition to the superiority of material, the PPT method is worth for investigating the optical properties of the thin film solar cell materials.

4. Conclusion

By using a PPT spectroscopy, that detects the nonradiative transition of photoexcited electrons, values of dE_{og}/dT of the DLC films deposited on quartz substrates were investigated. Since the PPT signal intensity is expected to be proportional to its optical absorption coefficient, the optical gap was estimated by a $(\mathrm{PPT}\ h\nu)^{1/2}$ plot. The observed dE_{og}/dT was found to be very small comparing with that of other semiconductor such as Si and GaAs. Since the dE_{og}/dT is an important parameter for improving the conversion efficiency of solar cells, obtained present results implies that the DLC films are excellent as the next generation solar cells materials. The device performance is expected to be very stable by temperature change.

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