

LOW TEMPERATURE ELECTRON PARAMAGNETIC RESONANCE STUDIES AND SPIN SUSCEPTIBILITY OF PHOSPHORUS-IMPLANTED C₆₀ FILMS FOR SOLAR CELLS

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ABSTRACT

Low temperature electron paramagnetic resonance (EPR) measurements have been made to clarify the origin and nature of paramagnetic electronic states responsible for the observed EPR signal in P⁺-implanted C₆₀ films. The data collected from the temperature dependence of the EPR signal intensity and the spin susceptibility revealed that the unpaired spin follows the Curie law at $T < 20 K$, while a clear deviation was observed at about $T > 20 K$. The temperature dependence of the linewidths indicates that the spin mobility occurs by hopping motion. In addition, the relation among defects, electrical, and optical properties was detected and analyzed. Finally, this study suggests that the transport mechanism occurs by hopping motion and the unpaired spins are partially localized.

INTRODUCTION

Since the discovery of a method for large-scale production of C₆₀ in 1985, the fullerenes have gained intensive investigations, reaching their climax when the 1996 Noble Prize for Chemistry was awarded to Kroto, Curl and Smally for their discovery. In reality, C₆₀ has several outstanding physical and chemical properties led many scientists to predict many technological applications. However, C₆₀ is a novel semiconductor with a direct energy gap ranging from 1.7 to 1.5 eV. Therefore, solid C₆₀ is expected to be a suitable material for the fabrication of solar cells. Unfortunately, the resistivity of C₆₀ film was about 10⁸ Ω.cm at room temperature, which makes C₆₀ electrically behave similar to a high resistivity semiconductor. Hence doping of C₆₀ is necessary for conductivity control and modification of its physical and chemical properties towards photovoltaic applications. Ion implantation is ideal technique for introducing dopants into C₆₀ fullerene. During ion bombardment of C₆₀ cage with

phosphorus ions a high density of structural defects are produced.

It is well known that the electron paramagnetic resonance (EPR) is a powerful technique in the identification and estimation of the paramagnetic defects and gives valuable information about the nature of the paramagnetic electronic states. The fundamental information of these defects in P⁺-implanted C₆₀ films was obtained through our previous EPR study [1]. Previous results showed that P⁺-implanted C₆₀ films have a high paramagnetic defect concentration of the order 10²¹ cm⁻³ with a g-value 2.0036. These defects are mainly originating from carbon dangling bonds in an amorphous layer introduced by P⁺-implantation of C₆₀. To make P⁺-implanted C₆₀ films photovoltaic grade material, a detailed study of the defect nature and their effects on the film properties are required. In deed, there are two main reasons for studying defects in P⁺-implanted C₆₀ films. The first reason is the improvement of the efficiency and performance of solar cells made from these films. The other reason is to study the phenomena associated with the presence of the defects such as these defects may be hopping sites for variable range hopping conductivity, which itself is very important phenomenon in disordered semiconductors. Accordingly, the purpose of the present work is to obtain more information about the nature of unpaired spins which responsible for the observed resonance. To achieve this, low temperature electron paramagnetic resonance measurements are performed. However, conduction mechanism was discussed through the temperature dependence of the linewidths. The relaxation times of carbon defects were included. In addition, correlation among paramagnetic defect, electrical and optical properties was discussed and presented.

EXPERIMENTAL

C₆₀ thin films were grown on coming glass 7059 substrate via molecular beam epitaxy (MBE) chamber under a base pressure of 2x10⁻⁹ Torr using pure C₆₀

powder (99.98 %). During the film deposition, the substrate temperature was kept constant at about 150 °C. The film thickness was measured using a Sloan Dek Tak surface profilometer and was found about 200 nm. The mass analyzed beam of positive phosphorus ions from a low energy Varian Extron implanter was used for the implantation experiments. Thin films of C₆₀ were implanted at room temperature with P⁺ ions of multiple energy (20-100 keV) and ion doses ranging from 1x10¹² to 5x10¹⁵ P⁺ ions cm⁻². The maximum energy affects the C₆₀ films to a depth of about 200 nm so that the substrate remains unaffected by the ion beam. EPR measurements were made in the temperature range from 4 to 300 K. Low temperature measurements were done in a controlled flow of liquid helium. The EPR measurements were performed using Bruker EMX Spectrometer operating in the X-band (9.4 GHz), 100 kHz field modulation. The g value, the linewidth, and the spin density were determined using the signal of Mn²⁺ in MgO as the calibration reference. Spin populations were calculated by comparing the integrated intensity of the signal with that of a standard Mn²⁺ in MgO. The spin-lattice (T₁) and spin-spin (T₂) relaxation times were estimated from the linewidth and saturation behavior. Magnetic susceptibility is proportional to the area under EPR absorption curve, and determined by double integrating of the experimental EPR signal.

RESULTS AND DISCUSSION

The temperature dependence of the EPR signal and the spin susceptibility are shown in Figs.1 and 2. Figure 1 shows that the EPR signal intensity, for films in the dose range from 1x 10¹² to 5x10¹⁵ P⁺ ions.cm⁻², abruptly increases at lower temperatures (T < 20 K). Figure 2 shows that, from one hand, the spin susceptibility obeys a Curie-Weiss law at sufficiently low temperatures (T < 20 K) according to [2]

$$C_{Curie} = \frac{n \cdot m_b \cdot m_B^2}{kT} \quad (1)$$

Where n is the density of the paramagnetic centers, m_b the Bohr magneton, m_o the permeability of the vacuum, k the Boltzman constant, and T the absolute temperature. The behavior of spin susceptibility at low temperatures can be attributed to the electrons of localized dangling bond defect states. On the other hand, a clear deviation from the Curie-like behavior was observed at T > 20 K. Indeed, for localized non-interacting spins a Curie-like behavior is expected, while for delocalized free (conduction) electrons the temperature independent Pauli paramagnetism should be observed. Therefore, the measurements of the temperature dependence of spin susceptibility should enable us to distinguish between localized and delocalized electrons. Obviously, from the analysis of the data in figures 1 and 2, we can distinguish between two

regimes in the temperature dependence of spin susceptibility. Firstly, at lower temperatures (T < 20 K), the films exhibit a 1/T behavior (i.e. Curie-like), which compacts from dangling bond electrons. While for second regime, at higher temperatures (T>20 K), the spin susceptibility deviates from Curie-law, and this trend can be understood in terms of excitation of the electrons into states either to band tails or extended states as those electrons become delocalized (overlap of spins wave function). This interpretation is consistent with conductivity measurements, which show a sharp increase in conductivity with increasing temperature, which will be published elsewhere.

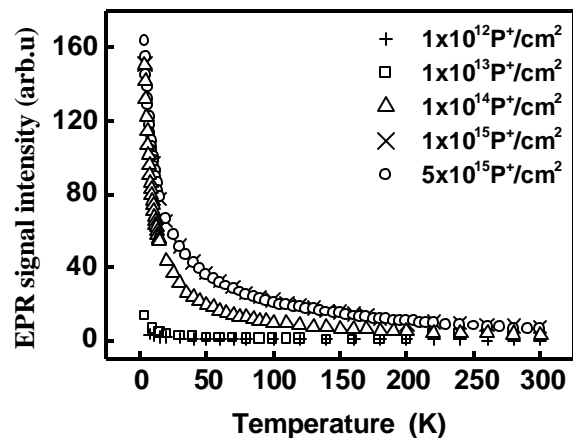


Fig. 1. Variation of EPR signal intensity as a function of temperature in P⁺-implanted C₆₀ films of doses from 1x10¹² to 5x10¹⁵ ions/cm² and multiple energies.

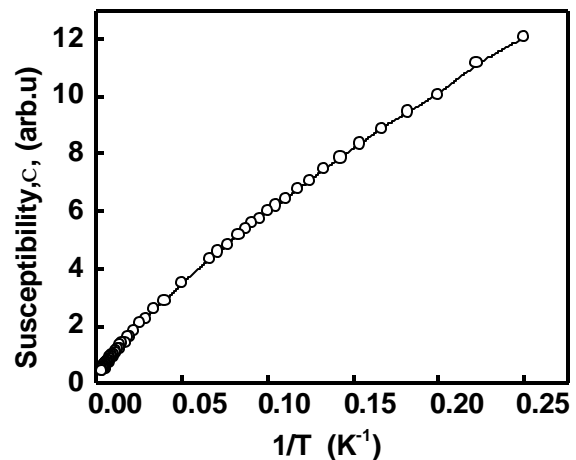


Fig. 2. Spin susceptibility of P⁺-implanted C₆₀ film implanted with dose of 5x10¹⁵ ions/cm² and multiple energies.

The temperature dependence of the EPR linewidths of P⁺-implanted C₆₀ films of doses 1x10¹², 1x10¹³, 1x10¹⁴, 1x10¹⁵, and 5x10¹⁵ P⁺ ions.cm⁻² is depicted in Fig. 3. In all films, except for low dose (1x10¹² P⁺ ions.cm⁻²), the linewidth of resonance narrows with increasing temperature up to T_{min}, which is the temperature at narrowest linewidth. In most films the temperature of the minimum is around 20 K, while in intermediate dose (1x10¹³ P⁺ ions.cm⁻²) it is around 100 -120 K. This minimum was mostly explained by averaging interaction either through exchange or motion of the electrons from one site to another (hopping conduction), which becomes less effective with decreasing temperature. The absence of the minimum in low dose film (1x10¹² P⁺ ions.cm⁻²) can be understood in term of spin density. This film has low spin density and consequently the distance between interacting spins becomes too large to allow for sufficiently rapid hopping motion or effective exchange interaction. On the other hand, the decrease of linewidth with increasing temperature (for T < T_{min}) was interpreted as a change in the correlation frequency of the exchange interaction due to the reduction of hopping rate of electrons between neighboring dangling bonds at lower temperatures. Interestingly, Yokomichi and Morigaki [3] explained the line broadening at low temperatures in fluorinated amorphous carbon films by the same reason. While, the increase in linewidth at higher temperatures with doping is consistent with the decrease in spin-lattice relaxation times with increasing implantation dose, as clear from figure 4.

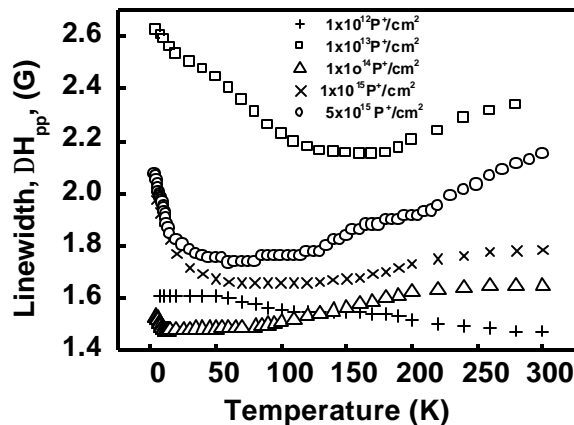


Fig. 3. Variation of EPR linewidth as a function of temperature in P⁺-implanted C₆₀ films of doses from 1x10¹² to 5x10¹⁵ ions/cm² of multiple energies.

In other words, to qualitatively report for the data of Fig. 3, we need to discuss spin-spin relaxation mechanisms, which determine the magnitude of the linewidth (ΔH_{pp}). We believe that additional spin-spin relaxation mechanism comes to play at low temperatures. One relevant relaxation mechanism at low temperatures is

the hopping of dangling bonds electrons from one site to another. In the case of hopping motion of electrons, the linewidth is inversely proportional to the probability p of the phonon-assisted transition from one center to another, (ΔH_{pp} ∝ 1/p). This probability depends on temperature by the following relation:

$$p \propto [\exp\{\frac{e_3}{kT}\}]^{-1} \quad (2)$$

Therefore, at low temperatures, where hopping is the dominant broadening mechanism, one should observe an increase in the linewidth as the temperature decreases, as suggested by our experimental results at T < 20 K. On the other hand, at higher temperatures (T > T_{min}), the dominant spin relaxation mechanism is the electron-phonon interaction and consequently the spin mobility reduced due to scattering effects [4]. Since the linewidth inversely proportional with the mobility, and then we can expect broadening of the linewidth at higher temperatures (T > T_{min}).

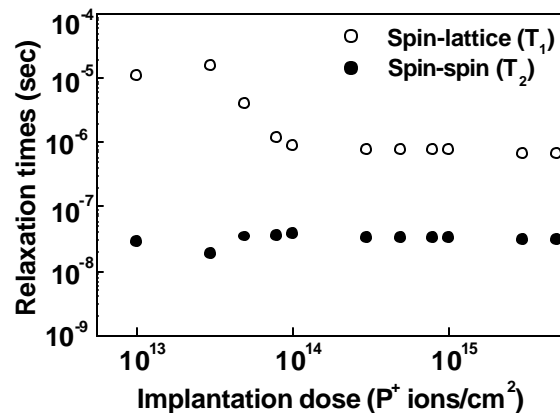


Fig. 4. Variation of spin-lattice (T₁) and spin-spin (T₂) relaxation times with phosphorus implantation dose (implantation condition: dose from 1x10¹³ to 5x10¹⁵ ions/cm² of multiple energy)

The close correlation between the dose dependence of the spin defect density and resistivity is shown in Fig.5. Clearly, the spin density increases from 4x10²¹ to 4x10²² p⁺ ions cm⁻² as a function of ion dose (1x10¹² to 5x10¹⁵). However, at low P⁺ ion doses ≤ 1x10¹³, the resistivity was high of the order >10⁷ Ω.cm. As the P⁺ doses increases to 5x10¹⁵ ions cm⁻², the resistivity is abruptly decreased to 0.5 Ω.cm due to the formation of amorphous carbon, which further supported by Raman spectra. Clearly, from mentioned results the ion implantation forms the amorphous carbon with high defect density (carbon dangling bonds). Hence the high defect density in the amorphous carbon leads to a decrease in the resistivity by

the hopping conduction. Furthermore, Figure 6 shows the variation of the EPR linewidth and the optical gap as a function of phosphorus ion dose. For doses $\geq 1 \times 10^{13}$ P⁺ cm⁻², their values sharply drop with P⁺ dose. In fact, both linewidth and optical gap strongly depend on the content and the cluster size of sp² sites, hence increasing sp² content is expected to increase the cluster size and decrease the optical gap. The reduction in linewidth as the sp² increases is associated with greater delocalization of the unpaired electrons as the cluster size increases. Therefore, greater delocalization leads to greater overlap of spin wave function and hence stronger exchange interaction.

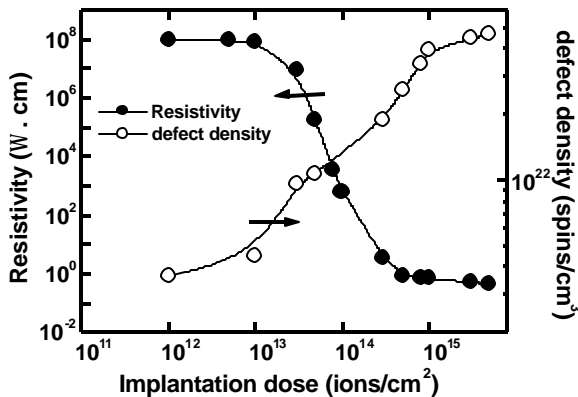


Fig. 5. Variation in resistivity and EPR defect density as a function of phosphorus implant ion dose (measured at room temperature).

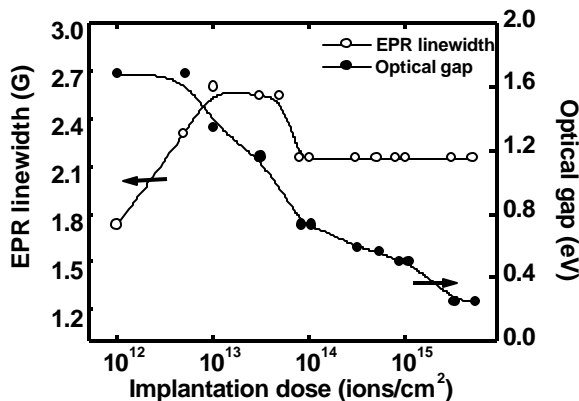


Fig. 6. Variation in optical gap and EPR linewidth as a function of phosphorus implant ion dose (measured at room temperature).

CONCLUSIONS

The temperature dependence of the electron paramagnetic resonance (EPR) parameters and spin magnetic susceptibility has been thoroughly studied and analyzed. The results allow us to identify the origin and the nature of the EPR signal, as well as the temperature dependence of the linewidth provides us with valuable information about the transport mechanism. At low temperatures ($T < 20$ K), the electrons giving rise to the ESR signal are localized at dangling bond center, leading to Curie-like behavior of the spin susceptibility. While at high temperatures ($T > 20$ K), a deviation from Curie law can be attributed to excitation of electrons into conduction band tails or/and extended states as those electrons become delocalized. However, the temperature dependence of the EPR resonance linewidth can be explained as follows: at low temperature ($T < T_{min}$), the linewidth narrows with increasing temperature, consistent with hopping motion of dangling bond electrons. While, at higher temperatures ($T > T_{min}$) the linewidth broadens due to electron-phonon interactions as a dominant spin-relaxation mechanism. Obviously, from spin relaxation times measurements, the narrowing effects exist for films of dose $\geq 1 \times 10^{13}$ P⁺ ions.cm⁻². From the close relation between the spin defect density and resistivity, it is clear that the defect density strongly affects on the electrical properties of the implanted films. The relation between optical gap and linewidth interpreted with changes in the structure of the films upon implantation.

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