Temperature dependence of electron spin resonance and electrical conductivity in P^+-implanted C_{60} films and their derivatives

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The temperature dependence of electron spin resonance (ESR) has been measured to clarify the origin and nature of paramagnetic states responsible for the observed ESR signal in P^+-implanted C_{60} films. Also, the temperature dependence of electrical conductivity was made and compared with ESR linewidths to detect the transport mechanism in these films. The ESR experiments were performed at 9.4 GHz in a wide temperature range from 3.7 to 300 K. The temperature dependence of the ESR signal intensity and spin susceptibility revealed that the unpaired spin follows the Curie law at $T<20$ K, while a clear deviation was observed at $T>20$ K. The Curie behavior of the spin susceptibility results from localized dangling bond electrons, while a deviation occurs due to delocalization and excitation of electrons into states as the temperature increases. The temperature dependence of linewidths indicates that the spin mobility occurs by hopping, taking into account that the electron–phonon interaction as spin relaxation mechanism at $T>T_{\min}$. The observed minimum in linewidths can be attributed to a decrease in the narrowing effects as the temperature decreases. Finally, the temperature dependence of the electrical conductivity and ESR resonance signal linewidth suggests that the transport mechanism occurs by hopping motion and the unpaired spins are partially localized. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1543243]

I. INTRODUCTION

Defect states in P^+-implanted C_{60} films are of great interest because not only do they remain elusive, but they also affect some electronic and optical properties of the material, as illustrated by its poor performance as the active layer in thin film solar cells.[1] Overall, the nature of the paramagnetic defects in the carbon-based materials is still far from clear. These could be both σ- and π-type defects but as Robertson and O'Reilly[2] have reported, π defects are expected to predominate due to their lower creation energy.

It is well known that the analysis of the temperature dependence of the electron spin resonance (ESR) signal gives useful information on the nature of the electronic states, their interactions with the lattice, and their mutual interactions. On the other hand, besides the nature of the defects, it is crucial to understand their behavior in the framework of the transport properties. Since the ESR linewidths are related with the spin relaxation times, the temperature trends of ESR linewidth are powerful tools to investigate the mobility processes of the unpaired electrons. Indeed, if the signals are hopping or motional narrowed, the linewidths decrease with temperature.

In addition, a study of the electrical conductivity as a function of temperature can yield valuable information regarding the electronic states and transport mechanism. However, insight on the structure of such a system can be given by the analysis of the conductivity, since the sp^3 phase is highly resistive and the sp^2 phase has energy levels near the Fermi level. Although, uncertainties still remain regarding the conduction mechanism in a-C:H and a-C materials there were some transport models that have been proposed, such as activated conductivity in delocalized states, hopping in band-tail states and at the Fermi level, multiphonon tunneling processes, and combination of these.[3] Furthermore, many authors reported that electrical conductivity is well fitted by the variable-range hopping,[4–6] $\sigma=\sigma_o \exp(T_o/T)^{1/4}$, at low temperatures, however, a better fit of experimental points by multiphonon tunneling was also demonstrated[7] in a-C.

In our previous ESR studies, the fundamental information about paramagnetic center in P^+-implanted C_{60} films was clarified.[8,9] The results showed that these films have a single Lorentzian line shape with g value 2.0036 ± 0.0004. We could not detect hyperfine splitting due to P^+ nucleus and therefore, we cannot claim its presence in the vicinity of the observed center. The spin density in the order of 10^{21} cm^{-3}, which was attributed to dangling bonds in an amorphous carbon layer introduced by P^+ implantation of C_{60} films at a sufficient phosphorus ion dose. This means that P^+ ions gradually transform crystalline C_{60} films into amorphous carbon at a sufficient ion dose and ion energy.[10,11] However, up to now, no low-temperature ESR measurements on P^+-implanted C_{60} films have been reported.

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In this article, we report low-temperature electron spin resonance (ESR) studies in P^+-implanted C_{60} films to clarify the origin and nature of paramagnetic spin, which is responsible for the observed ESR signal. Also, related variations in ESR parameters (signal intensity, linewidths, and ESR susceptibility) were detected and analyzed. Finally, the data were correlated with electrical conductivity measurements and from their analysis, the nature of the resonance and the spin transport mechanism were determined.

II. EXPERIMENTAL DETAILS

A. Sample preparation

C_{60} thin films were grown on Corning glass 7059 and quartz substrates by molecular beam epitaxy (MBE) under a base pressure of 2×10^{-9} Torr using high purity C_{60} powder (99.98%). During the film deposition, the substrate temperature was maintained at about 150 °C. The film thickness was measured using a Sloan Dektak surface profilmeter and was found about 200 nm. The mass analyzed beam of positive phosphorus ions from a low energy Varian Extrion implanter was used for the implantation experiments. Thin films of C_{60} were implanted at room temperature with P^+ ions of multiple energies (20–100 keV) and ion doses ranging from 1×10^{12} to 5×10^{15} P^+ ions cm^{-2}. The maximum energy affects the C_{60} films to a depth of about 200 nm so that the substrate remains unaffected by the ion beam.

B. ESR characterization

ESR measurements were made in the temperature range from 3.7 to 300 K. Low temperature measurements were done in a controlled flow of liquid helium in ESR 900 cryostat under vacuum of 10^{-5} Torr. The ESR measurements were performed using Bruker EMX Spectrometer operating in the X-band (9.4 GHz), 100 kHz field modulation. The spin-lattice (T_1) and spin–spin (T_2) relaxation times were estimated from the linewidth and saturation behavior.[12] Magnetic susceptibility is proportional to the area under the ESR absorption curve, and determined by double integration of the experimental ESR signal. For conductivity measurements, evaporated gold electrodes were used in a gap cell configuration and silver paste was used as a point contact on gold electrodes. The electrical conductivity of the films was measured, as a function of temperature from 20 to 350 K in helium gas atmosphere with flow of liquid helium in spectrostat CF. Ohmic behavior was controlled by measuring current–voltage characteristics at ambient temperature and at higher temperature as well. For $T<20$ K the conductivity was below our detection limit. For low doses films, as the temperature decreases the conductivity becomes below the detection limit.

III. RESULTS AND DISCUSSION

A. Signal intensity and spin susceptibility

The temperature dependence of the ESR signal and spin susceptibility are shown in Figs. 1 and 2, respectively. Figure 1 shows that the ESR signal intensity, for films in the dose range from 1×10^{12} to 5×10^{15} 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[13] at sufficiently low temperatures ($T<20$ K) according to

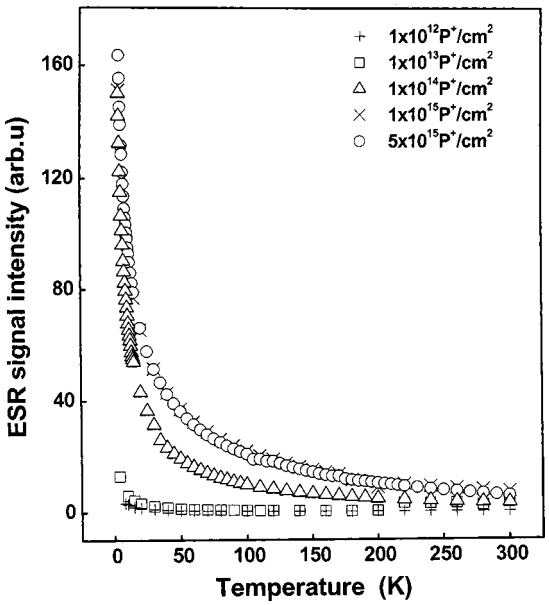

FIG. 1. Variation of ESR signal intensity as a function of temperature in P^+-implanted C_{60} films of doses from 1×10^{12} to 5×10^{15} ions/cm^2 and multiple energies.

$$\chi_{\text{Curie}}=\frac{n.\mu_o.\mu_B^2}{kT}, \tag{1}$$

where n is the density of the paramagnetic centers, μ_B the Bohr magneton, μ_o the permeability of the vacuum, k the Boltzmann 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

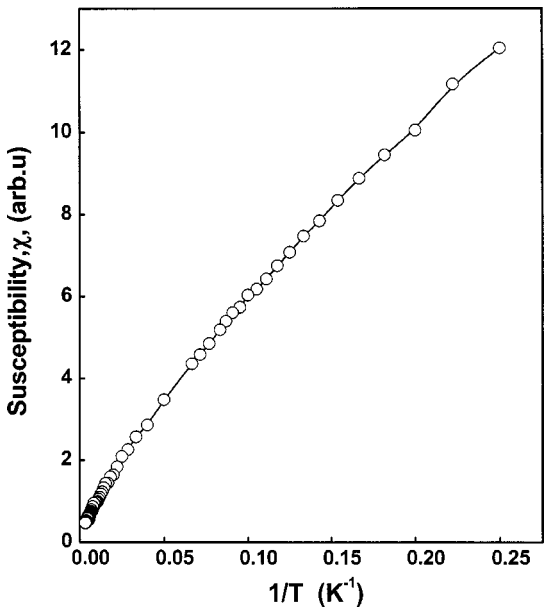

FIG. 2. Spin susceptibility of P^+-implanted C_{60} film implanted with dose of 5×10^{15} ions/cm^2 and multiple energies.

states. On the other hand, a clear deviation from the Curie-like behavior was observed at higher temperatures ($T > 20$ K). Indeed, for localized noninteracting 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 Figs. 1 and 2, we can distinguish between two regimes in the temperature dependence of spin susceptibility. At lower temperatures ($T < 20$ K), the films exhibit a $1/T$ behavior (i.e., Curie-like), which results from dangling bond electrons. 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). The analysis of the spin susceptibility data shows that spin susceptibility in P^+-implanted C_{60} films consists of two components: Curie-like behavior ($T < 20$ K) + non-Curie behavior ($T > 20$ K). The non-Curie behavior can be understood in terms of rising temperature leads to an increasing number of electrons excited into states. This indicates the excitation of electrons into states leading to a deviation from $1/T$ behavior. However, at the present time additional information about spin susceptibility at high temperature cannot be totally ruled out on the basis of the data available. Since the electrons contributing in the resonance did not form free electron, we could not expect Pauli-like susceptibility. This interpretation is consistent with conductivity measurements, which show a sharp increase in conductivity with temperature. However, Golzan[14] observed Curie behavior for temperature from 100 to 150 K for *t a*-C films.

B. ESR linewidths

Figure 3 shows the temperature dependence of the ESR linewidths of P^+-implanted C_{60} films of doses 1×10^{12}, 1×10^{13}, 1×10^{14}, 1×10^{15}, and 5×10^{15} P^+ ions cm^{-2}. In all films, except for low dose (1×10^{12} P^+ ions cm^{-2}), the linewidth of resonance narrows with raising 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 (1×10^{13} 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 (1×10^{12} P^+ ions cm^{-2}) can be understood in terms 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 ($T < T_{min}$) 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.

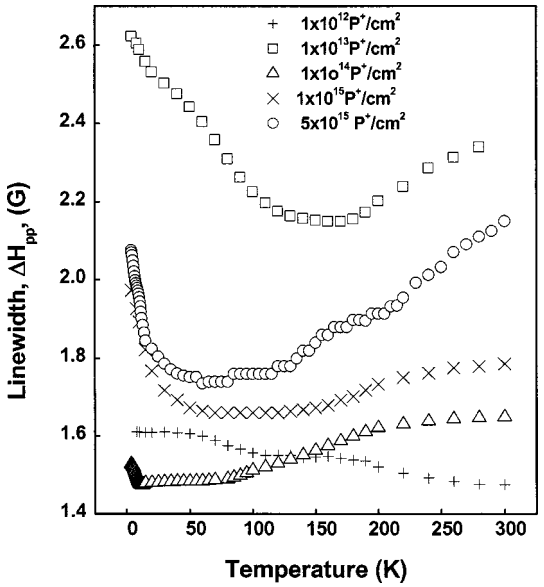

FIG. 3. Variation of ESR linewidths as a function of temperature in P^+-implanted C_{60} films of doses from 1×10^{12} to 5×10^{15} ions/cm^2 of multiple energies.

Interestingly, Yokomichi and Morigaki[15] explained the line broadening at low temperatures in fluorinated amorphous carbon films by the same reason. Also, Müller *et al.*[16] reported that as one goes to very low temperatures, the narrowing effect becomes weaker resulting in an overall increase in linewidth and leading to the observed minimum. A decrease in linewidth with increasing temperature ($T < T_{min}$) has been observed for donors in III–V semiconductors, e.g., P in Si, As in Ge.[17–19] While, the increase in linewidth at higher temperatures with doping is consistent with the decrease in spin-lattice relaxation times as implantation dose increases, as clear from Fig. 4.

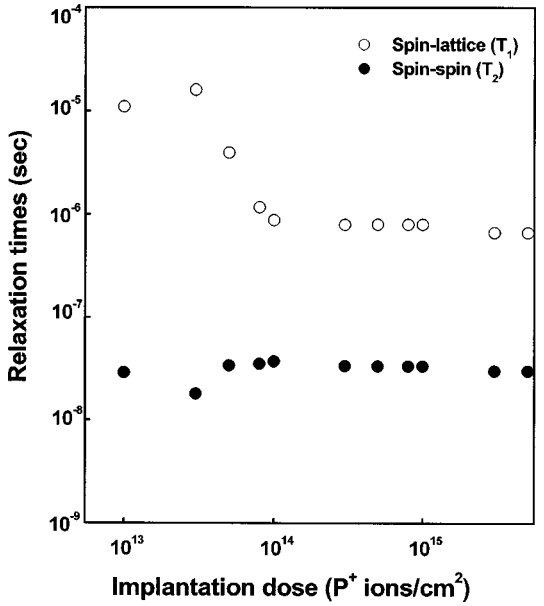

FIG. 4. Variation of spin-lattice (T_1) and spin–spin (T_2) relaxation times with phosphorus implantation dose (implantation condition: dose from 1×10^{13} to 5×10^{15} ions/cm^2 of multiple energies).

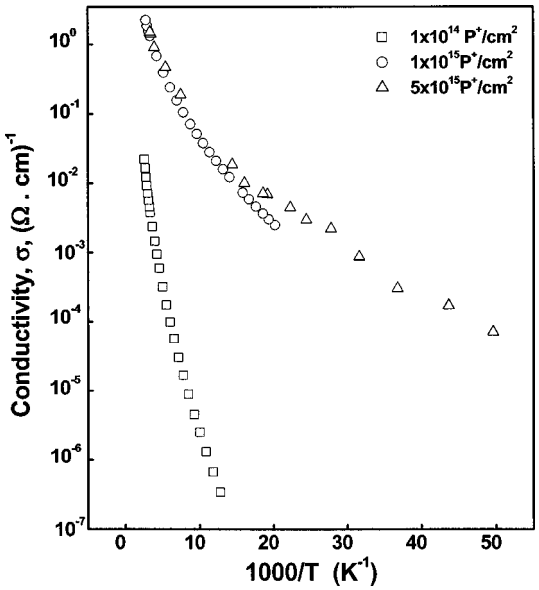

FIG. 5. Temperature dependence of dc electrical conductivity in $(T)^{-1}$ scale for P^+-implanted C_{60} films of different doses and multiple energies.

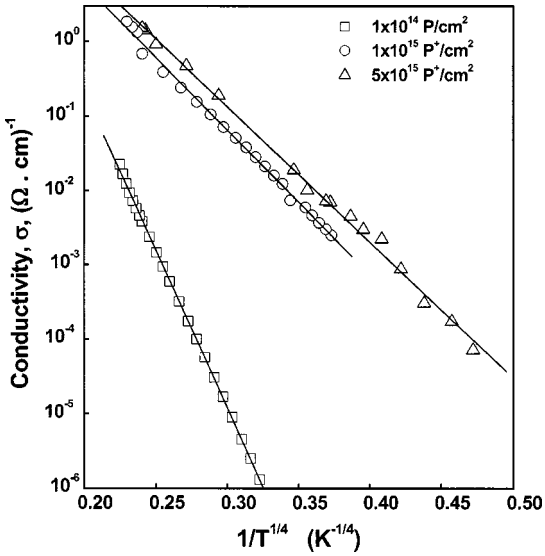

FIG. 6. Temperature dependence of dc electrical conductivity in $(T)^{-1/4}$ plot for P^+-implanted C_{60} films of different doses and multiple energies (solid lines referred to the linear fitting).

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. Such a process was observed to be the dominant line broadening mechanism at low temperatures in heavily doped *n*-type silicon.[20] Our conductivity data have indicated hopping conduction in the investigated films, which will be discussed. 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 ($\Delta H_{pp} \propto 1/P$). This probability depends on temperature by the following relation:[21,22]

$$p \propto [\exp(\varepsilon_3/kT)^{-1}]^{-1}. \tag{2}$$

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 contrary, at higher temperatures ($T>T_{\min}$), the dominant spin relaxation mechanism is the electron–phonon interaction and consequently the spin mobility is reduced due to scattering effects.[23] Since the linewidth is inversely proportional with the mobility, then we can expect broadening of the linewidth at higher temperatures ($T>T_{\min}$). However, Giorgis and Tagliaferro[24] reported that the increase of linewidth with temperature in "*sp a*-C" is connected with extended states mobility.

C. Conductivity

Arrhenius plot ($\log \sigma \propto 1000/T$) for the conductivity of three of the investigated films of doses 1×10^{14}, 1×10^{15}, and 5×10^{15} P^+ ions cm^{-2} are shown in Fig. 5. Clearly, the measured data curves continuously in the whole temperature range, and the curvature is dependent on the dose of each film. In fact, if these films follow the Arrhenius function:

$$\sigma_{dc}(T) = \sigma_0 \exp(-E_\sigma/k_B T), \tag{3}$$

they should give a linear dependence in this plot, and the activation energy (E_σ) can be determined from the slope of that linear part. Consequently, P^+-implanted C_{60} films do not exhibit Arrhenius-type behavior in the temperature range from 20 to 300 K. This means the conduction does not obey activated behavior.

The data in Fig. 5 are replotted on $T^{-1/4}$ temperature scale as shown in Fig. 6. The data are quite well fitted between 20 and 300 K by the relation:

$$\sigma_{dc}(T) = \sigma_0 \exp[-(T_0/T)^{1/4}]. \tag{4}$$

This trend suggests a hopping conductivity similar to that found in other amorphous semiconductors (Ge, Si, and Sb).[25] Previous articles have thrown some light on the mechanisms of conduction in *a*-C at low temperatures[26] and *a*-C and *a*-C:H above 270 K.[27] These studies have shown that at very low temperatures ($T<20$ K) variable-range hopping is dominant in graphite-like amorphous carbon,[26] while the proposed mechanism at room temperature was conduction in band tails for low Tauc gap (less than 0.8 eV).

Now, we discuss the transport mechanism in terms of temperature dependence of ESR linewidths. Indeed, in the presence of a hopping mechanism for conductivity, the temperature dependence of the linewidth can be related to the hopping frequency as follows:

$$\Delta H_{pp}(T) \propto \upsilon^{-1}{}_{\text{hop}}. \tag{5}$$

Since υ_{hop} is activated, a decrease of linewidth as temperature increases is expected. This is in good agreement with our experimental results at low temperatures region ($T<20$ K), while in disagreement with results obtained at higher temperatures ($T>20$ K). To explain this behavior, at

higher temperature, from susceptibility data we can understand that above $T>20$ K the electrons are not localized, which due to the strong overlap between states. Accordingly, we expect the conduction occurs by hopping of carriers in band tails and/or extended states at $T>T_{min}$. However, from the susceptibility data and the temperature dependence of the ESR linewidth, we can expect that the apparent temperature dependence of the conductivity does not relate to conduction by variable range hopping of carriers in localized band near the Fermi level rather it is probably due to conduction by hopping of carriers in band tails and /or extended states.[23,28] Demichelis *et al.*[23] referred the decrease in the linewidth with temperature in the case of *a*-C:H to conduction by hopping mechanism in the whole temperature range. Also, he reported that the increase in the linewidth with the temperature, in the case of *a*-C films, is attributed to conduction by extended states, or at least overlapping states. However, the trends of temperature dependence of linewidth and conductivity at $T>20$ K are consistent with the high spin density, which causes overlap of paramagnetic spins wave functions. However, the decrease of the conductivity with a lowering of temperature was ascribed both to the decrease in the number of electrons excited into states and to the reduction in the hopping rates between dangling bond electrons as the distance increases between hopping sites. Clearly, from the above discussion, the temperature dependence of conductivity and ESR linewidth data indicates a hopping rather than activated conduction.

IV. CONCLUSIONS

The temperature dependence of the ESR signal and the electrical conductivity in a series of P^+-implanted C_{60} films has been thoroughly studied and analyzed. The results allow us to identify the origin and the nature of the ESR signal, as well as establish a relation between ESR and transport data. 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 and/or extended states as those electrons become delocalized. However, the temperature dependence of the ESR resonance linewidth can be explained as follows: at low temperature ($T<T_{min}$), the linewidth narrows as temperature increases, which 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. The observed minimum in linewidth for most of the films is ascribed to the decrease in the narrowing effects as one goes to low temperatures. Obviously, from spin relaxation times measurements, the narrowing effects exist for films of dose $\geqslant 1\times10^{13}$ P^+ ions cm^{-2}. Furthermore, the comparison of the temperature dependence of the electrical conductivity and the ESR resonance signal linewidth indicates the following: (a) at low temperature ($T<20$ K), the transport mechanism is due to hopping of dangling bond electrons, (b) at higher temperatures ($T>20$ K), the spin mobility is probably attributed to hopping of carriers in delocalized conduction band tails and /or extended states, besides this consideration the electron–phonon interaction as a dominant spin relaxation mechanism in this temperature range, as suggested by our spin susceptibility and ESR linewidth data.

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[1] K. L. Narayanan and M. Yamaguchi, J. Appl. Phys. **89**, 8331 (2001).
[2] J. Robertson and E. P. O'Reilly, Phys. Rev. B **35**, 2946 (1987).
[3] A. Helmbold, P. Hammer, J. U. Thiele, K. Rohwer, and D. Meissner, Philos. Mag. B **72**, 335 (1995).
[4] C. J. Adkins, S. M. Feake, and E. M. Hamilton, Philos. Mag. **22**, 183 (1970).
[5] J. J. Hauser, Solid State Commun. **17**, 1577 (1975).
[6] M. Morgan, Thin Solid Films **7**, 313 (1971).
[7] K. Shimakawa and K. Miyake, Phys. Rev. Lett. **61**, 994 (1988).
[8] N. F. Fahim, N. Kojima, M. Yamaguchi, Y. Ohshita, A. E. Eid, and N. Dharmarasu, Sol. Energy Mater. Sol. Cells **75**, 411 (2002).
[9] N. F. Fahim, N. Kojima, M. Yamaguchi, Y. Ohshita, N. Dharmarasu, and T. Sakai, in Proceedings of 12th International Photovoltaic Science and Engineering Conference, Jeju Island, Korea, June, pp. 121.
[10] K. L. Narayanan, O. Goetzberger, A. Khan, N. Kojima, and M. Yamaguchi, Sol. Energy Mater. Sol. Cells **65**, 29 (2001).
[11] N. Dharmarasu, T. Sakai, N. Kojima, M. Yamaguchi, Y. Ohshita, and K. L. Narayanan, J. Appl. Phys. **89**, 318 (2001).
[12] P. C. Poole, *Electron Spin Resonance- A Comprehensive Treatise on Experimental Techniques*, 2nd ed. (Wiley Interscience, New York, 1983), Chap. 13, pp. 589.
[13] N. M. Atherton, *Principles of Electron Spin Resonance* (Prentice-Hall, New York, 1993).
[14] M. M. Golzan, D. R. McKenzie, D. J. Miller, S. J. Collocott, and G. Amaratunga, Diamond Relat. Mater. **4**, 912 (1995).
[15] H. Yokomichi and K. Morigaki, J. Non-Cryst. Solids **266–269**, 797 (2000).
[16] J. Müller, F. Finger, R. Carius, and H. Wagner, Phys. Rev. B **60**, 11666 (1999).
[17] J. D. Lépine, Phys. Rev. B **2**, 2429 (1970).
[18] S. Maekawa and N. Kinoshita, J. Phys. Soc. Jpn. **20**, 1447 (1965).
[19] E. M. Gershenzon, N. M. Pevin, and M. S. Fogelson, Phys. Status Solidi **38**, 865 (1970).
[20] B. G. Zhurkin, N. A. Penin, and P. Swarup, Fiz. Tverd. Tela (Leningrad) **8**, 3550 (1966) [Sov. Phys. Solid State **8**, 2839 (1966)].
[21] N. F. Mott and W. D. Twose, Adv. Phys. **10**, 107 (1961).
[22] A. Miller and E. Abrahams, Phys. Rev. **120**, 745 (1960).
[23] F. Demichelis, C. Demartino, A. Tagliaferro, and M. Fanciulli, Diamond Relat. Mater. **3**, 844 (1994).
[24] F. Giorgis and A. Tagliaferro, Amorphous Carbon: State of the Art, pp. 143–162 (1998).
[25] J. J. Hauser, Solid State Commun. **17**, 1577 (1975).
[26] J. Hauser, J. Non-Cryst. Solids **23**, 21 (1977).
[27] D. Dasgupta, F. Demichelis, and A. Tagliaferro, Philos. Mag. B **63**, 1255 (1991).
[28] S. H. Moustafa, M. Koós, and I. Pócsik, J. Non-Cryst. Solids **227–230**, 1087 (1998).