Plasma-Polymerized Hexamethyldisiloxane Films Characterized by Variable-Energy Positron Lifetime Spectroscopy

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ABSTRACT: Nanometer-size holes in plasma-polymerized thin films were characterized by variable-energy positron lifetime spectroscopy for the first time. Hexamethyldisiloxane (HMDSiO) was plasma-polymerized at different discharge powers (30–105 W) and monomer pressures (1.0–4.9 Pa). The positron lifetime spectra of deposited films were collected at positron energies of 1 and 5 keV. All films showed a well-defined long-lived component due to pick-off annihilation of *ortho*-positronium (*o*-Ps). The *o*-Ps lifetime τ_3, reflecting the average size of free-volume holes in the film, increased with an increasing ratio of plasma discharge power, W, and monomer flow rate, F. Based on the empirical relationship between the *o*-Ps lifetime and the cavity radius, hole volumes were estimated to be 0.19–0.36 nm^3. We also found that the *o*-Ps intensity, I_3, depends strongly on the same parameter, W/F. Comparison with infrared (IR) absorption spectroscopy data showed that Ps formation is suppressed in films with fewer organic bonds and higher disorder, i.e., those increasingly inorganic in nature. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2522–2528, 1999

Key words: plasma-polymerized film; hexamethyldisiloxane; variable-energy positron lifetime spectroscopy

INTRODUCTION

Polymers formed in monomer gas glow discharge have superior thermal stability, high melting points, and low solubility.[1] Complex plasma reactions produce polymer films structurally distinct from conventionally polymerized counterparts. Active radicals formed in the glow discharge may react directly with each other to form a polymeric molecule or transfer energy to the substrate or polymer surface to form surface radicals, which also contribute to polymerization.[2] The resultant film is believed to have no discernible repeating units and to contain complicated highly cross-linked, highly branched networks.[3]

We applied positron annihilation lifetime spectroscopy (PALS) to characterizing nanometer-size holes in plasma-polymerized thin films. PALS is used to study free volume and defects in materials. A fraction of the positrons injected into a polymeric system combines with an electron to form the bound state, positronium (Ps), either in spin–antiparallel *para* (*p*-) or spin-parallel *ortho* (*o*-) states. A typical positron lifetime spectrum of a polymer thus contains three exponentially decaying components, mainly due to the self-annihilation of *p*-Ps, free positron annihilation, and pick-off annihilation of *o*-Ps localized in a nanom-

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eter-size hole. In 1981 an empirical relationship between the *o*-Ps pick-off annihilation lifetime and free-volume cavity size was introduced by Eldrup et al.,[4] making it possible to quantify the free-volume hole size in different substances.[5] The cavity volume deduced from this simple relationship correlates well with diffusion coefficients of argon, nitrogen, and oxygen in different polymers,[6] demonstrating the usefulness of Ps as a probe for studying free volume in polymers.

In conventional PALS, energetic positrons from a radioactive source such as ^{22}Na are directly injected into samples. The mean implantation depth of positrons cannot be controlled, and only bulk information can be obtained for millimeter-thick samples. The development of pulsed positron beams with variable energy enabled PALS to be applied to depth-selective quantitative analysis of defects in materials such as thin films.[7–12] We applied variable-energy PALS to characterize the microstructure of plasma-polymerized hexamethyldisiloxane (HMDSiO) thin films, a material attracting attention for potential use in gas separation membranes,[13] oxygen barrier coatings,[14] and coatings protective against oxidative plasma etching.[15]

EXPERIMENTS

Plasma polymerization was conducted in a cylindrical glass reactor about 4 cm in diameter and 60 cm long, similar to one described elsewhere.[15] The reactor is connected through a cold trap to an evacuation system consisting of a rotary pump, a diffusion pump, and a pair of vacuum gauges.

HMDSiO was purchased from Tokyo Chemical Industry Ltd. (Japan) and used without further purification. After air was removed from HMDSiO by vacuum freeze-thawing, the reactor was evacuated to a vacuum exceeding 0.01 Pa, and monomer vapor was introduced through a needle valve. Under a steady flow of HMDSiO at a constant vapor pressure (P), electrodeless glow discharge plasma was generated at an inductively coupled radiofrequency (RF) of 13.56 MHz, supplied by a JEOL JEH-005TS RF power supply through an impedance matching circuit. Monomer pressure was controlled by adjusting the needle valve opening and was measured using an MKS Baratron gauge. Monomer flow rate, F, was estimated from the pressure increase in the reactor after the evacuation valve was closed. The flow rate was found to be proportional to $P^{1.6}$. A number of films were deposited on Si (100) substrates placed 27 cm downstream from the discharge zone center under different RF discharge powers (30–105 W) and monomer pressures (1.0–4.9 Pa). Films were kept in a vacuum for at least 6 h before PALS measurement.

Positron lifetimes were measured using the intense pulsed positron beam at the Electrotechnical Laboratory (ETL). Positrons generated with a linear accelerator were converted to a DC beam from which positron pulses with a time spread of about 100 ps were produced by chopping and bunching. Lifetime spectra were measured by determining the interval between the timing signal from the pulsing system and the detection of an annihilation γ-ray by a BaF_2 scintillation detector, as detailed elsewhere.[8] Positron lifetimes were measured under a vacuum of 10^{-6} Pa at positron energies of $E = 1$ keV and 5 keV, for which mean positron implantation depths were about 0.0040 and 0.053 mg/cm^2.[16] About 1 million counts were accumulated in 10–15 min. Some films were not thick enough to stop all positrons with an energy of 5 keV. For such films, only data at 1 keV are reported.

Polymerized film chemical structures were studied using infrared (IR) absorption spectroscopy of films deposited on Si wafers and recorded at room temperature with a Perkin Elmer Spectrum-2000 having a resolution of 4 cm^{-1}. Spectra were analyzed by plotting absorption coefficient, $\alpha(\omega)$, versus radiation frequency, ω, after correction for coherent multiple reflections. Film thickness, d, and refractive index, n, were estimated from the period and amplitude of fringes of baseline transmission (for details, see references[17–19]). The IR spectrum of the monomer was obtained using a pair of KBr discs as a substrate.

RESULTS

Infrared Spectroscopy

IR transmission spectra (raw data) for plasma films deposited at monomer pressures of 4.7 and 1.3 Pa with a discharge power of 100 W are shown, along with the monomer spectrum, in Figure 1. Absorption bands were observed around 1,258 cm^{-1}, 1,035 cm^{-1}, 840 cm^{-1}, and 756 cm^{-1}—the first two due to Si—CH_3 and Si—O—Si, and the last two to Si—$(CH_3)_3$.[14,15] Despite the presence of these common bands, noticeable differences occurred among the three spectra: (1)

two film spectra have an additional peak at about 800 cm^{-1} due to the Si—$(CH_3)_2$ bond[14,15,20]; (2) most peaks in the film spectra are considerably broader than the monomer spectrum; and (3) relative intensities, widths, and positions of many peaks differ among the three spectra. These results indicate significant structural differences among the monomer and plasma-polymerized films.

To get more quantitative information from IR spectra, the following quantities were evaluated[17–19]: (1) integrated absorbance, I, of absorption peaks in $\alpha(\omega)$ via $I = \int \alpha(\omega)/\omega d\omega$,[18] (2) peak position, ω_0,[21] and (3) width, Γ, of peaks in the imaginary part of the refractive index, $k(\omega)$,[21] which correlates with $\alpha(\omega)$ as $\alpha(\omega) = 4\pi k(\omega)\omega$. We calculated these for the well-separated peak of Si—O—Si around 1035 cm^{-1} based on a least-squares analysis. Figure 2 shows variations of the integrated absorbance, width and position of the Si—O—Si peak as a function of $W/P^{1.6}$, which is proportional to power input divided by monomer flow rate (W/F).

As the ratio of the plasma discharge power to the flow rate increases, so does the Si—O—Si peak intensity (Fig. 2). This is consistent with observations by Park and Kim,[20] indicating that many carbon atoms are removed from films prepared at high ratios of plasma discharge power to flow rates. The Si—O—Si peak becomes broader and shifts downward, indicating that the film structure becomes increasingly heterogeneous with increasing $W/P^{1.6}$.[20,21]

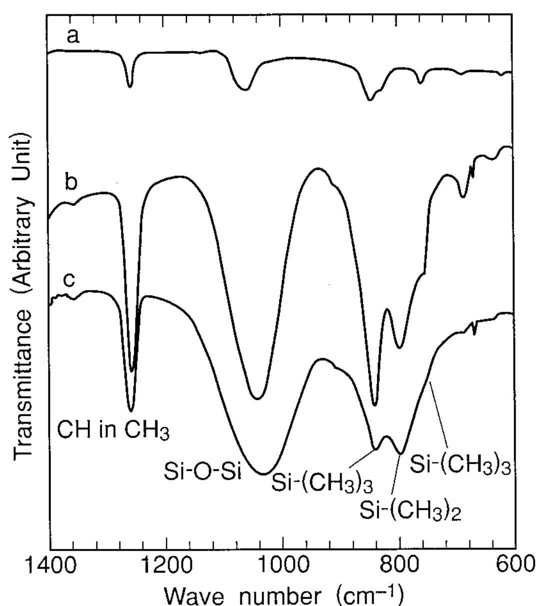

Figure 1 Infrared spectra (raw data) of (a) monomer, (b) plasma film deposited at 100 W and 4.7 Pa, and (c) plasma film deposited at 100 W and 1.3 Pa.

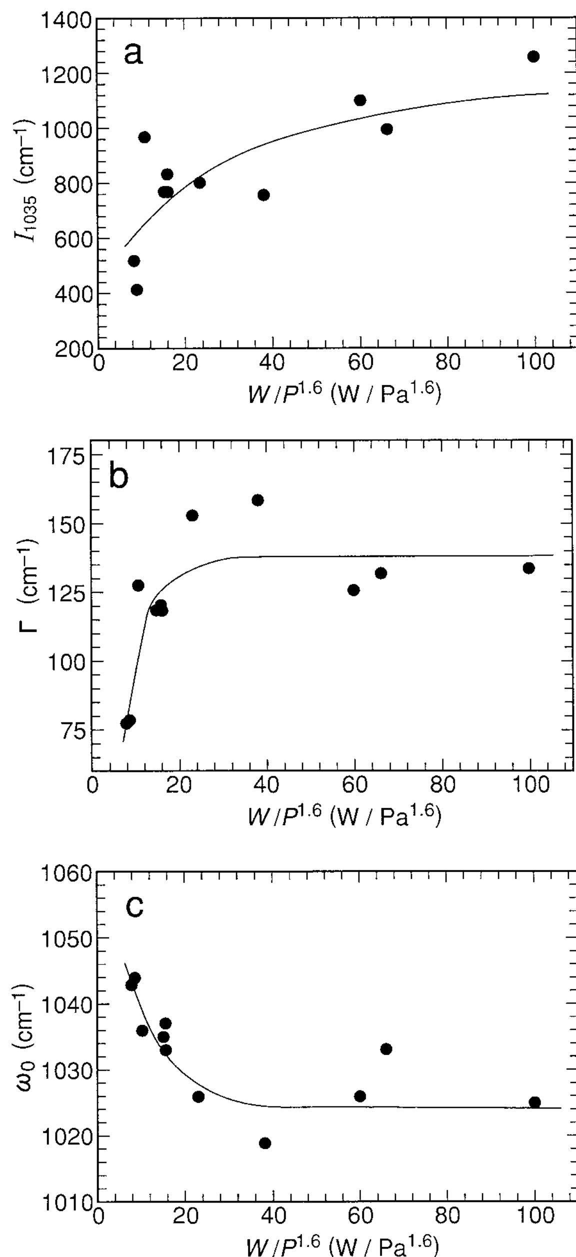

Figure 2 Effect of parameter, $W/P^{1.6}$ (proportional to power per monomer flow rate, W/F), on the IR absorption peak at 1,035 cm^{-1} (Si—O—Si): (a) integrated absorbance, I_{1035}; (b) width, Γ; (c) central peak position, ω_0. These parameters were evaluated by approximating the absorption peak as a single Gaussian.

Positron Annihilation Lifetime Spectroscopy

In typical positron lifetime spectra of plasma-polymerized HMDSiO films (Fig. 3), a well-defined

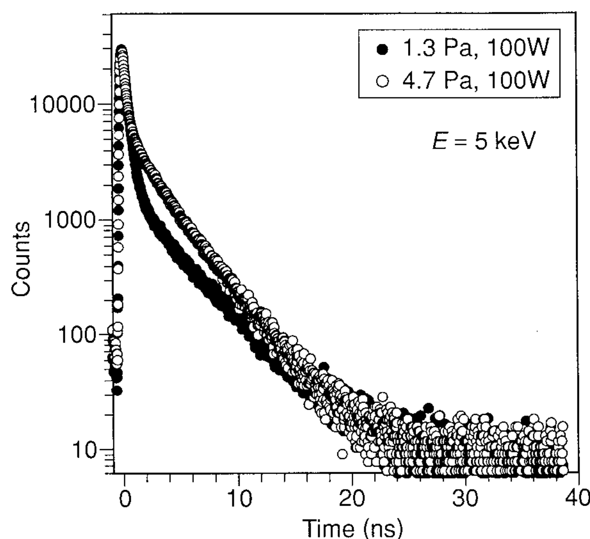

Figure 3 Typical positron lifetime spectra of plasma-polymerized HMDSiO films. The two curves are normalized at the same peak count to show the difference clearly.

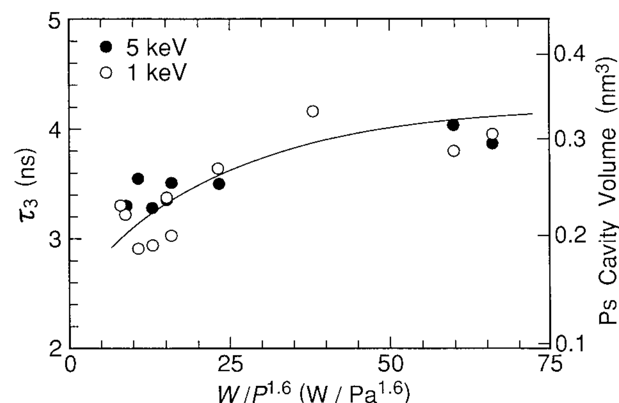

Figure 4 Variation of *o*-Ps lifetime τ_3 versus ratio $W/P^{1.6}$.

long-lived component was seen because of *o*-Ps pick-off annihilation. To obtain numerical values of *o*-Ps lifetime parameters, we analyzed lifetime spectra in three exponential components using the PATFIT-88 program.[22] The *o*-Ps lifetime (τ_3) and intensity (I_3) for some of the samples thus deduced are listed in Table I. Also included in Table I are data for polydimethylsiloxane (PDMS) by conventional positron lifetime spectroscopy.[23] The lifetime and intensity of the *o*-Ps component for sample 4, prepared at a monomer pressure of 4.7 Pa and a power of 100 W, are very similar to PDMS (τ_3 = 3.41 ns, I_3 = 44.2%). However, the lifetime parameters in other films differ from PDMS, and the microstructure of each film depends strongly on polymerization conditions such as monomer pressure and discharge power.

Figure 4 shows τ_3 as a function of $W/P^{1.6}$ for all films studied by PALS. The pick-off annihilation lifetime τ_3 becomes progressively longer with increasing $W/P^{1.6}$. As *o*-Ps lifetime increases with increasing free-volume cavity size, the correlation (Fig. 4) indicates that the larger the energy input per monomer, the larger the cavity.

According to Eldrup et al.,[4] the pick-off annihilation lifetime of *o*-Ps is related to free-volume cavity size as follows:

$$\tau_3 = 0.5(\text{ns})\{1 - (R/R_0) + 0.159 \sin(2\pi R/R_0)\}^{-1} \quad (1)$$

Here $R = R_0 - \Delta R$ is the cavity radius and $V_c = (4\pi/3)R^3$ is the cavity volume. This relationship is based on a simple model in which Ps resides in an infinite spherical potential of radius R_0 with an electron layer having a thickness ΔR. ΔR was chosen to be 0.166 nm by Nakanishi et al.,[5] so that eq. (1) reproduces known hole volumes of zeolites and other substances. The same choice of ΔR gives hole volumes shown on the

Table I Comparison of *o*-Ps Lifetime Parameters at *E* = 5 keV in Some Plasma-Polymerized HMDSiO Films Prepared Under Different Conditions

Sample	P (Pa)	W (W)	d (μm)	n	τ_3 (ns)	I_3 (%)
1	1.2	80	1.49	2.92	4.03	29.7
2	1.3	100	0.94	2.52	3.87	25.6
3	1.7	30	0.89	2.90	3.28	27.5
4	4.7	100	1.41	2.11	3.30	46.0
PDMS					3.41*	44.2*

Statistical error ranges for τ_3 are 0.01–0.03 ns and for I_3 0.1–0.3%. Note thickness, d, and refractive index, n, of each film estimated from the IR transmission spectrum.

* Conventional PALS.[23]

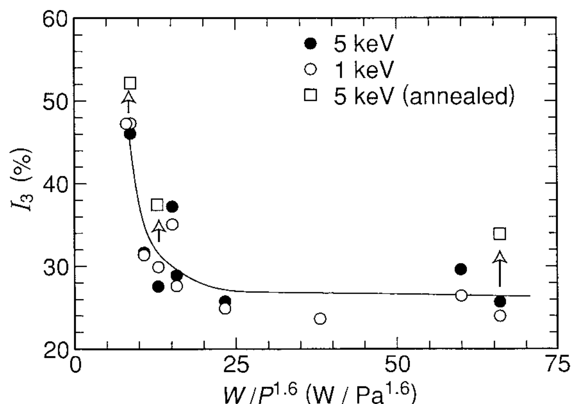

Figure 5 Variation of *o*-Ps intensity, I_3, versus $W/P^{1.6}$. Solid circles denote data for as-deposited films at positron energies for 5 keV and open circles for 1 keV. Squares denote data for films annealed at 400°C and measured at a positron energy of 5 keV. Arrows indicate the relative I_3 change between as-deposited and annealed samples.

right-hand scale in Figure 4. The cavity volume ranged from 0.19 to 0.36 nm^3, much larger than that for polyethylene and other carbon-based polymers.[6] The presence of such large cavities may account for the high gas permeability of plasma-polymerized HMDSiO films reported by Yamamoto et al.[13]

Returning to Table I, we see not only the *o*-Ps lifetime but also its intensity varies from one film to another. The *o*-Ps intensity in films prepared under high $W/P^{1.6}$ ratios is much lower than those prepared at lower $W/P^{1.6}$ (Fig. 5). The implications of this observation are not so straightforward as to lifetime because the Ps formation probability in polymers is known to be influenced by several factors.

DISCUSSION

Park and Kim[20] showed that many experimental results on HMDSiO plasma polymerization are understandable with the activation-growth model. According to this model, plasma polymer chemical structure is controlled by the monomer fragmentation pattern. Because the activation of a monomer into reactive fragments is governed by the specific energy received per unit molecule (W/F), the chemical structure of plasma polymer presumably depends strongly on this parameter. Many properties of plasma-polymerized HMDSiO films have been confirmed to systematically change with W/F; for instance, film density increases with W/F and ranges between PDMS (0.98 g/cm^3) and SiO_2 or SiC (above 2 g/cm^3).

Given the activation-growth model, it may not be surprising that the hole volume determined from the *o*-Ps lifetime as well as the *o*-Ps intensity I_3 varies with W/F. A gradual increase in hole volume shows that local packing density of the film probed by Ps decreases, even though overall macroscopic density increases. Li et al.[24] saw a somewhat similar increase in hole volume for a conventional polysiloxane upon curing. In contrast to *o*-Ps lifetime variation, the implication of the correlation between I_3 and $W/P^{1.6}$ (Fig. 5) is not straightforward because Ps formation in polymers is influenced by several different effects.

According to the spur reaction or diffusion-recombination model,[25,26] Ps is formed by a reaction between a positron and an electron, ionized from medium molecules by the positron itself, in the terminal positron spur (blob). Ps formation in the positron blob is influenced by other processes, such as electron–ion recombination, positron and electron scavenging (trapping) by defects, free radicals, polar groups, and so forth. If, for example, a positron or an electron is captured by defects or other trapping centers, due to its reduced diffusion length, positron–electron recombination becomes less probable, and Ps formation is suppressed.[27–29]

Plasma polymer contains an appreciable number of trapped free radicals due to the activation–growth nature of polymerization.[20] To study the effect of trapped radicals on I_3, three films prepared at $W/P^{1.6}$ = 8.7, 13, and 66 W/Pa$^{1.6}$ were annealed at 400°C in a vacuum and slowly cooled to room temperature, and PALS measurement was conducted. The I_3 thus obtained was 6–10% higher than before annealing (Fig. 5). As trapped radicals in plasma-polymerized HMDSiO film disappear at about 300°C,[30] the above results indicate that the presence of radicals somewhat reduces Ps formation. The increase in I_3 after annealing at 400°C, however, is about the same for all three films studied, and the observed large variation of I_3 from one film to another cannot be explained. We therefore relate the variation of I_3 to the change in film structure shown by IR spectroscopy.

The IR result [Fig. 2(a)] shows that numbers of Si—O—Si bonds increase with the power flow rate ratio and support the observation by Yasuda[31] and Park and Kim[20] that, with increasing W/F, the structure of the plasma polymer gradu-

ally changes from that similar to PDMS to a dense covalent network less organic in nature. Such gradual change of structure should reduce Ps formation, provided that a long-lived *o*-Ps atom is formed in the less dense polymerlike part of the film but not in the high-density network mainly composed of Si—O—Si.[32] The *o*-Ps lifetime in pure SiO_2 is reported to be only 1.6–1.8 ns.[33] Alternatively, within the framework of the spur reaction model, the reduced intensity in the film prepared at higher $W/P^{1.6}$ can be related to its more inhomogeneous nature [Fig. 2(b) and (c)]. The blob positron or electron may be trapped by a potential produced by the irregular arrangements of the chemical bond, suppressing positron–electron recombination in the terminal positron spur. The relative contribution of the above two possible effects is not very clear, but the correlation between I_3 and $W/P^{1.6}$ (Fig. 5) is consistent with the activation–growth mechanism of plasma polymerization.

CONCLUSION

We measured the lifetime of *o*-Ps and its formation probability in a series of plasma-polymerized HMDSiO films using variable-energy PALS and found that lifetime gradually increases and intensity gradually decreases with the increasing ratio of plasma discharge power (W) to monomer flow rate (F). Based on an empirical relationship between the *o*-Ps lifetime and the free-volume hole size, the cavity volumes were estimated to be 0.19–0.36 nm^3. A suitable combination of monomer pressure and discharge power thus makes it possible to grow a HMDSiO film with a desired average hole volume in this range. The observed reduction of the *o*-Ps intensity with increasing W/F was related to the increasingly inorganic nature of the film and the formation of a more disordered structure rather than the presence of trapped free radicals. Our results demonstrate the usefulness of variable-energy PALS in studying nanometer-size holes in plasma-polymerized thin films.

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REFERENCES

1. Millard, M. In Techniques and Applications of Plasma Chemistry; Hollahan, J. R.; Bell, A. T., Eds., Wiley: New York, 1974.
2. Plasma Chemistry; Polak, L. S.; Lebedev, Y. A., Eds., Cambridge International Science Publishing: Cambridge, 1998, Chapter 6.
3. Yasuda, H. J Membr Sci 1984, 18, 273.
4. Eldrup, M.; Lightbody, D.; Sherwood, J. N. Chem Phys 1981, 63, 51.
5. Nakanishi, H.; Wang, S. J.; Jean, Y. C. In International Symposium on Positron Annihilation Studies of Fluids; Sharma, S. C., Ed., World Scientific: Singapore, 1987.
6. Kobayashi, Y.; Haraya, K.; Hattori, S.; Sasuga, T. Polymer 1994, 35, 925.
7. Schödlbauer, D.; Sperr, P.; Kögel, G.; Triftshäuser, W. Nucl Instrum Meth Phys Res B 1988, 34, 258.
8. Suzuki, R.; Kobayashi, Y.; Mikado, T.; Ohgaki, H.; Chiwaki, M.; Yamasaki, T.; Tomimasu, T. Jpn J Appl Phys 1991, 30, L532.
9. Suzuki, R.; Kobayashi, Y.; Mikado, T.; Matsuda, A.; McElheny, P. J.; Mashima, S.; Ohgaki, H.; Chiwaki, M.; Yamasaki, T.; Tomimasu, T. Jpn J Appl Phys 1991, 30, 2438.
10. Suzuki, R.; Kobayashi, Y.; Mikado, T.; Ohgaki, H.; Chiwaki, M.; Yamasaki, T.; Uedono, A.; Tanigawa, S.; Funamoto, H. Jpn J Appl Phys 1992, 31, 2237.
11. Suzuki, R.; Mikado, T.; Ohgaki, H.; Chiwaki, M.; Yamasaki, T.; Kobayashi, Y. Phys Rev B 1994, 49, 17484.
12. Xu, J.; Somieski, B.; Hulett, L. D.; Pint, B. A.; Tortorelli, P. F.; Suzuki, R.; Ohdaira, T. Appl Phys Lett 1997, 71, 3165.
13. Yamamoto, M.; Sakata, J.; Hirai, M. J Appl Polym Sci 1984, 29, 2981.
14. Agres, L.; Segui, Y.; Delsol, R.; Raynaud, P. J Appl Polym Sci 1996, 61, 2015.
15. Hirotsu, T.; Nugroho, R. J Appl Polym Sci 1997, 66, 1049.
16. Vehanen, A.; Saarinen, K.; Hautojarvi, P.; Huomo, H. Phys Rev B 1987, 35, 4606.
17. Maley, N. Phys Rev B 1992, 46, 2078.
18. Langford, A. A.; Fleet, M. L.; Nelson, B. P.; Lanford, W. A.; Maley, N. Phys Rev B 1992, 45, 13367.
19. Manfredotti, C.; Fizzotti, F.; Boero, M.; Pastorino, P.; Polesello, P.; Vittone, E. Phys Rev B 1994, 50, 18046.
20. Park, S. Y.; Kim, N. J Appl Polym Sci Appl Polym Symp 1990, 46, 91.
21. Ossikovski, R.; Drévillon, B. Phys Rev B 1996, 54, 10530.
22. Kirkegaard, P.; Pedersen, N. J.; Eldrup, M. PATFIT-88; Risoe National Laboratory: Roskilde, Denmark, 1989.
23. Wästlund, C.; Maurer, F. H. J Nucl Instrum Meth Phys Res B 1996, 117, 467.
24. Li, H. L.; Ujihira, Y.; Yoshino, T.; Yoshii, K.; Yamashita, T.; Horie, K. Polymer 1998, 39, 4075.

25. Mogensen, O. E. Positron Annihilation in Chemistry; Springer-Verlag: Berlin, 1995.
26. Byakov, V. M.; Stepanov, S. V. J Radioanal Nucl Chem 1996, 210, 371.
27. Kobayashi, Y.; Zheng, W.; Hirata, K.; Suzuki, T. Radiat Phys Chem 1997, 50, 589.
28. Kobayashi, Y.; Wang, C. L.; Hirata, K.; Zheng, W.; Zhang, C. Phys Rev B 1998, 58, 5384.
29. Wang, C. L.; Hirade, T.; Maurer, F. H. J.; Eldrup, M.; Pedersen, N. J. J Chem Phys 1998, 108, 4654.
30. Morinaka, A.; Asano, Y. J Appl Polym Sci 1982, 27, 2139.
31. Yasuda, H. Plasma Polymerization; Academic Press: New York, 1985.
32. Li, H. L.; Ujihira, Y.; Nakamura, T.; Ryuo, T. Nippon Kagakukaishi 1995, 2, 128 (in Japanese).
33. Hasegawa, M.; Tabata, M.; Miyamoto, T.; Nagashima, Y.; Hyodo, T.; Fujinami, M.; Yamaguchi, S. Mater Sci Forum 1995, 175–178, 269.