Materials Letters 63 (2009) 1594–1597

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Synthesis of radio frequency plasma polymerized non-synthetic Terpinen-4-ol thin films

K. Bazaka, M.V. Jacob *

Electronic Materials Research Lab, School of Engineering, James Cook University, Townsville QLD 4811, Australia

ARTICLE INFO

Article history:
Received 20 February 2009
Accepted 9 April 2009
Available online 21 April 2009

Keywords:
Plasma polymerization
Thin film
Optical properties
Organic polymer

ABSTRACT

Recent advancements in the area of organic polymer applications demand novel and advanced materials with desirable surface, optical and electrical properties to employ in emerging technologies. This study examines the fabrication and characterization of polymer thin films from non-synthetic Terpinen-4-ol monomer using radio frequency plasma polymerization. The optical properties, thickness and roughness of the thin films were studied in the wavelength range 200–1000 nm using ellipsometry. The polymer thin films of thickness from 100 nm to 1000 nm were fabricated and the films exhibited smooth and defect-free surfaces. At 500 nm wavelength, the refractive index and extinction coefficient were found to be 1.55 and 0.0007 respectively. The energy gap was estimated to be 2.67 eV, the value falling into the semiconducting E_g region. The obtained optical and surface properties of Terpinen-4-ol based films substantiate their candidacy as a promising low-cost material with potential applications in electronics, optics, and biomedical industries.

1. Introduction

Surface engineering is one of the most prominent areas of materials research and development and is widely implemented over a broad range of possible applications, to considerably improve performance and to add to the value of material manufacturing, and significant importance is placed on process and product innovation and cost management [1–5]. With regard to manufacturing, plasma based technologies are growing rapidly in terms of industrial application as they are highly engineering-friendly, deliver practically pollutant free surface chemistry, and can be easily integrated into manufacturing processes [2,3]. Early applications of plasma polymers made use of the physical nature of these highly cross-linked materials, the barrier properties in particular, and included electronics, metal coatings and membranes. With subsequent identification of non-equilibrium plasma conditions capable of delivering chemically functionalized polymer thin films with retention of some of the original chemistry and structure of the monomer and the inherent advantages of the substrates (e.g. their mechanical properties), the range of applications broadened from permselective membranes to include biomedical films [5,6]. Typically, the resulting thin films are characterized by smooth surface, ultrathin, pin-hole free films possessing spatial uniformity, conformal coverage and high adhesion to the substrate [7–12].

With an ever increasing demand for novel low-cost materials with specific electrical and optical properties for use in many emerging technologies, a number of organic materials have been examined as potential candidates for electronics and biomedical applications [1–5,13]. Radio frequency (RF) polymerization is one of the most commonly used deposition methods for fabrication of thin films from a wide array of organic materials, including the ones that do not contain the type of functionalities normally associated with conventional polymerization. The goal of this study was to evaluate non-synthetic material as a suitable source for RF polymerization of organic thin films with desirable optical and electrical properties. This paper reports on the fabrication of polymer thin films from non-synthetic Terpinen-4-ol derived from *Melaleuca alternifolia* by means of RF plasma polymerization and optical, electrical and surface characterization of the polymer thin films.

2. Materials and methods

RF polymerization process has been discussed in detail by many authors [1–6,13]. During the polymerization, the energy levels of particles that amass the gas within a deposition chamber increase significantly resulting in electrons being released and charged heavy particles (molecular and atomic species) formed [14]. The energy of most electrons is enough to break virtually any chemical linkage pertinent to organic molecules and organic structures containing main group elements, with higher energies needed to dissociate unsaturated bonds. A result of the plasma state processes, the high molecular weight networks generated from collisions and subsequent recombination of the charged and neutral species with each other and the surfaces that constrain the discharge, possess structural attributes that significantly differ from the ones of the original monomer. Such structures are not built from repeating monomer units and are likely to possess unsaturated, branched and cross-linked architecture. Conventional polymer formation employs plasma-generated functionalities

* Corresponding author. Tel.: +61 7 47814379; fax: +61 7 47815177.
E-mail address: Mohan.Jacob@jcu.edu.au (M.V. Jacob).

0167-577X/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2009.04.025

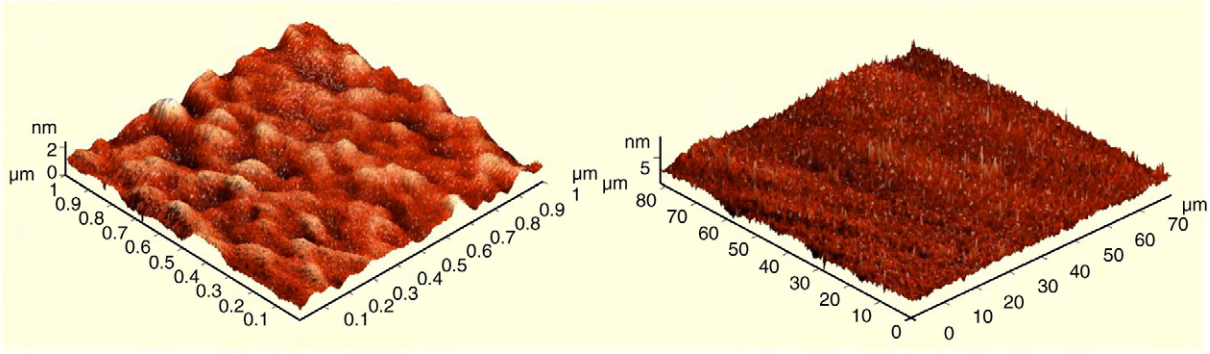

Fig. 1. AFM picture of film fabricated at 25 W, scan size 1×1 μm and 80×80 μm.

and radicals, however the process takes place in the absence of plasma on plasma exposed substrate surfaces [1–6,13]. It is possible to control polymer material characteristics by changing the deposition conditions (e.g. power and frequency of the excitation signal, type and position of the substrate, geometry of the deposition chamber) or applying prior and post deposition treatments (e.g. subjecting the substrates to prefabrication RF plasma treatment) [1,2,5,13,15].

A custom-manufactured glass deposition chamber [16] was used to fabricate the RF polymer thin films from Terpinen-4-ol monomer (supplied by Australian Botanical Products). Copper electrodes are capacitively coupled to the reactor so that RF (13.56 MHz) energy is delivered into the deposition chamber. The distance between the electrodes was varied to achieve optimal deposition conditions. A number of substrate cleaning processes were carried out. First, of all the superwhite glass substrates (25 mm×75 mm) were washed in a solution of Extran and distilled water. Secondly, the substrates were subjected to 30 min ultrasonic clean in distilled water heated to 50 ° C followed by a Propan-2-ol rinse and air-dry. The cleaned glass substrate was placed into the deposition chamber and the chamber was flushed with argon for 1 min. The monomer was released gradually into the chamber kept at a pressure of 150 mTorr — the glow was maintained by controlling the monomer flow by means of a vacuum stop cock. Deposition was performed at room temperature, pressure of 200 mTorr and RF power of 25 W. For every deposition, 1 ml of monomer was used.

3. Results and discussion

3.1. Film thickness

A spectrometer (Avantes 2048) was employed for preliminary investigations of the polymer films' absorbance and thickness. These parameters were also evaluated using a variable angle spectroscopic ellipsometer (model M-2000, J. A. Woollam Co., Inc.). The dependence of film thickness on the deposition time was studied on samples fabricated on the glass substrates for 2, 5, 10, 15, 20, and 30 min (4 samples for each deposition time). A film thickness of 99 nm was obtained with deposition time of 2 min. The sample thickness increased with time, approaching 874 nm for deposition time of 30 min. Linear thickness dependence on deposition time was observed. Therefore, assuming constant deposition conditions, the desired film thickness can be obtained by controlling the time of deposition so that the material can be tailored for a given application.

3.2. Surface properties

The surface morphology of the films was investigated using atomic force microscope (NT-MDT NTEGRA Prima) to understand topographical properties of the surfaces over scales ranging from angstroms to microns [13]. The non-destructive semi-contact AFM mode was chosen to minimize the damage to the surface of the films. A number of scans were performed on each sample to improve the accuracy of characterizations. Fig. 1 shows an example of the surface morphology of 1×1 μm and 80×80 μm scans of the Terpinen-4-ol polymer thin film of thickness 874 nm. The results confirmed the polymer thin films as smooth, uniform and pin-hole free surface, implying that the plasma polymerization has taken place mostly on the surface of the substrate and not in the gas phase [17]. The RMS roughness of 0.3 nm obtained from the AFM data was in agreement with the value obtained from the ellipsometric studies of the films. Such roughness values are below those for thiophene and ethylcyclohexane polymer films, 1 nm and 1.2 nm respectively, deposited using RF plasma polymerization [18,19]. Smooth surfaces are vital for optical and electrical applications, and also for implementing as a coating materials for surface protection or buffer layers [5].

3.3. Optical properties

Optical properties of the films were derived from the ellipsometric data collected at three different angles of incidence ($\varphi = 55°$, 60°, and 65°) over the wavelength range of 200–1000 nm (6.2–1.2 eV) by means of regression analysis (WVASE32 software package). First, Cauchy dispersion was applied to data within 500–1000 nm range assuming the films are optically transparent within this region (k approximates 0) and the film is homogenous [20,21]. A surface roughness layer was employed assuming the roughness being less

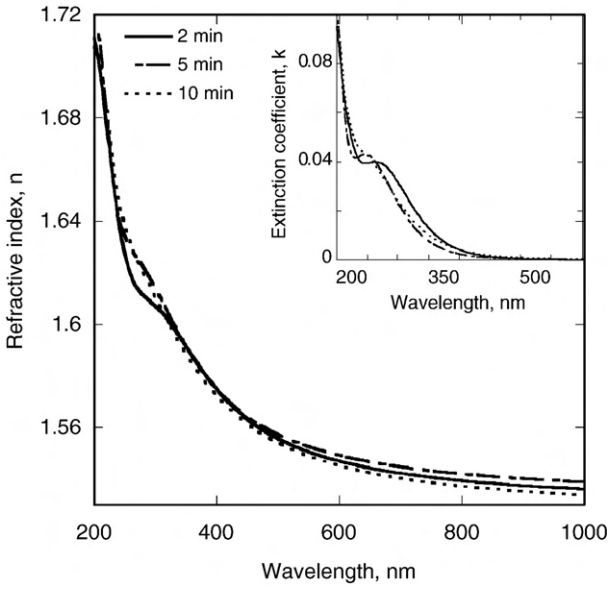

Fig. 2. Refractive index and extinction coefficient as a function of wavelength.

than 10% of the wavelength of the light used in probing the sample as greater roughness has a propensity to scatter and depolarize light [22]. Further, Gaussian oscillators were employed as harmonic oscillators [23,24]. Transmission data was appended to enhance the accuracy of the model used to determine optical constants of the material and understand the transparency range of the polymer films under investigation. The refractive index and extinction coefficient values range from 1.71 to 1.53 (Fig. 2) and from 0.1 to 4×10^{-7} (Fig. 2, inset) respectively over the wavelength region of 200 to 1000 nm. The effect of deposition time on the refractive index and extinction coefficient was insignificant with all curves exhibiting similar shape. Mean squared error (*MSE*) values used to assess the quality of the fit were below 3, and although it is preferential to have *MSE* values as close to zero as possible. *MSE* value tend to vary significantly depending on factors such as the amount and quality of the data available, or how precisely the chosen model mirrors the thin films under investigation [25]. UV–Vis absorption spectra of the samples deposited at 25 W RF power and 200 mTorr were studied. As is shown in Fig. 3, the polymer thin film was optically transparent across the deposition time range (Fig. 3). As an optically transparent film, the material can find its application as an encapsulating (protective) layer for the circuit boards.

3.4. Energy gap

Energy gap estimates derived from ellipsometric and spectrometric data analyses were compared and conclusions on the conducting nature of the material were drawn. The optical band gap E_g is derived from the Tauc equation $\alpha h\nu = B\ (h\nu - E_g)^n$, where α is the optical absorbance, ν is the frequency of light, and n and B are factors dependant on the type of transition and the length of localized state tails respectively [26]. The value of n is determined by the nature of the electronic structure of the material, with semiconducting plasma polymers generally attracting n of 2 which describes a parabolic function for the density of states [27]. Matlab software was employed to calculate the optical band gap values by extrapolating the linear section of the absorption curve to the abscissa (Fig. 4). $n=2$ (for indirect transition) were shown to provide the best fit for the polymer films under investigation [9]. The energy gap values (2.67 eV and 2.66 eV for UV–Vis spectrometric and ellipsometric data respectively) exhibit that the optical band gap of the material was in the semiconducting region. With addition of doping materials, for example iodine or bromine, it would be possible to further lower the energy gap of the material making the film conducting. Although the optical band gap deviates from the value of E_g by the width of the range of localized states in the valence or conduction band, the degree of variation being dependent on the degree of disorder within the polymer film [28], this method provides important information about the electronic structure of amorphous materials [29]. Using the WVASE32 software, a combination of Tauc–Lorenz and Gaussian oscillators was fitted to the ellipsometric data during modeling to ascertain the values of E_g. An energy gap value of 2.68 eV was achieved in this study. This value is similar to the values obtained using the ellipsometric and spectroscopic UV–Vis absorption data and it falls within the semiconducting region of E_g.

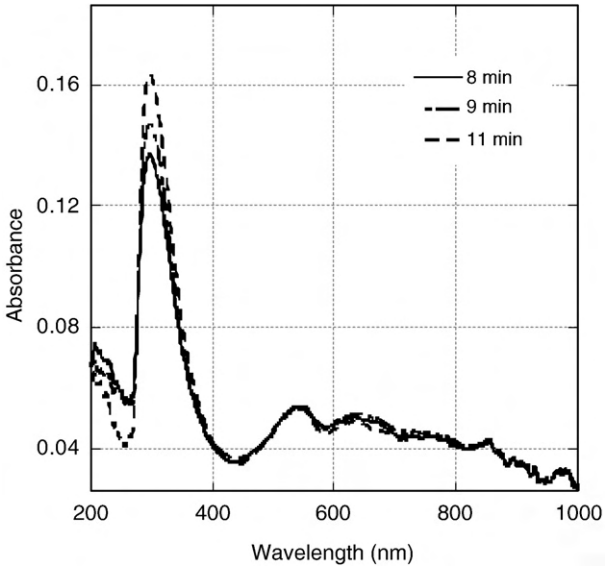

Fig. 3. UV–Vis absorption spectrum of film deposited at RF power of 25 W.

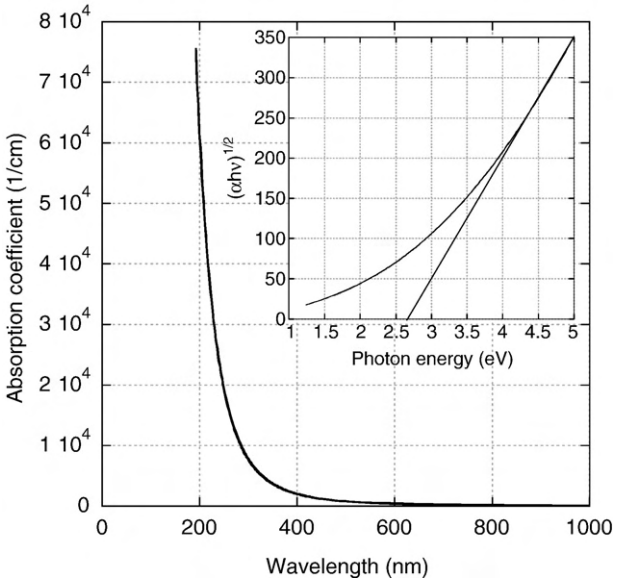

Fig. 4. Absorption coefficient as a function of wavelength of film deposited at 25 W.

4. Conclusions

The RF plasma polymerization of Terpinen-4-ol monomer was studied with the objective to synthesize a smooth, defect-free and homogenous film from a non-synthetic source. UV–Vis, ellipsometry, and AFM characterizations demonstrated the plasma conditions had effect on morphology and properties of the resultant film. Transparent, smooth and uniform organic polymer films can be manufactured using RF excitation signal of 13.56 MHz and power of 25 W. The thickness could be varied from 100 nm to 1000 nm by controlling the deposition time. The optical properties studied in the wavelength range 200–1000 nm identified the films as potential candidates for applications in optics. At 500 nm wavelength, the refractive index and extinction coefficient were found to be 1.55 and 0.0007 respectively. The energy gap estimated to be 2.67 eV confirmed the possibility of using the polymer film in semiconducting applications.

The obtained optical and surface properties of the fabricated films substantiate the candidacy of the material as a promising low-cost environmentally friendly material that could be used in many emerging technologies. We demonstrated the ability to manufacture uniform, defect-free non-synthetic Terpinen-4-ol based films with desirable material properties in a reliable and reproducible fashion and their potential as candidates for electronics, optics, and biomedical industries applications.

Acknowledgments

KB is grateful to the APA and AINSE scholarships. Authors are also grateful to the funding and support obtained from RIRDC and the AFM facilities of JCU AAC.

References

[1] Biederman H, Slavínská D. Surf Coat Technol 2000;125(1–3):371–6.
[2] Denes FS, Manolache S. Prog Polym Sci 2004;29(8):815–85.
[3] Forrest SR. Nature 2004;428(6986):911–8.
[4] Muccini M. Nat Mater 2006;5(8):605–13.
[5] Shi FF. Surf Coat Technol 1996;82(1–2):1–15.
[6] Yasuda H. J Polym Sci: Macromol Rev 1981;16(1):199–293.
[7] Hiratsuka A, Karube I. Electroanalysis 2000;12(9):695–702.
[8] Kim MC, Cho SH, Han JG, Hong BY, Kim YJ, Yang SH, et al. Surf Coat Technol 2003;169–170:595–9.
[9] Sajeev U, Mathai C, Saravanan S, Ashokan R, Venkatachalam S, Anantharaman M. Bull Mater Sci 2006;29(2):159–63.
[10] Yasuda H, Hsu T. J Polym Sci Polym Chem Ed 1977;15(1):81–97.
[11] Yasuda H, Yu Q. Plasma Chem Plasma Process 2004;24(2):325–51.
[12] Mathai CJ, Saravanan S, Jayalekshmi S, Venkitachalam S, Anantharaman MR. Mater Lett 2003;57(15):2253–7.
[13] Johnston EE, Ratner BD. J Electron Spectrosc Relat Phenom 1996;81(3):303–17.
[14] Biederman H, Osada Y. Plasma polymerization processes. New York: Elsevier Science Publications; 1992.
[15] Bae IS, Cho SJ, Choi WS, Hong BY, Kim YJ, Kim YM, et al. Thin Solid Films 2008;516(11):3577–81.
[16] Jacob MV, Easton CD, Woods GS, Berndt CC. Thin Solid Films 2008;516(12):3884–7.
[17] Hu X, Zhao X, Uddin A, Lee CB. Thin Solid Films 2005;477(1–2):81–7.
[18] Deposition and basic properties of thiophene plasma polymer films. In: Polonskyi O, Matousek J, Drabik M, Kousal J, Choukourov A, Slavinska D, et al, editors. WDS'08 Proceedings of Contributed Papers, Part III; 2008. MATFYZPRESS.
[19] Cho SH, Park ZT, Kim JG, Boo JH. Surf Coat Technol 2003;174–175:1111–5.
[20] Rochotzki R, Arzt M, Blaschta F, Kreyig E, Poll HU. Thin Solid Films 1993;234(1–2):463–7.
[21] Wang G, Gan F. Mater Lett 2000;43(1–2):6–10.
[22] Jaglarz J, Wagner T, Cisowski J, Sanetra J. Optical Materials 2007;29(7):908–12.
[23] Campoy-Quiles M, Etchegoin PG, Bradley DDC. Synth Met 2005;155(2):279–82.
[24] Jellison JGE, Modine FA. Appl Phys Lett 1996;69(3):371–3.
[25] Woollam Co. Inc JA. Guide to using WVASE32; 2001.
[26] Tauc J, Menth A, Wood DL. Phys Rev Lett 1970;25(11):749.
[27] Mujahid M, Srivastava DS, Gupta S, Avasthi DK. Radiat Phys Chem 2005;74(2):118–22.
[28] Davis EA, Mott NF. Philos Mag 1970;22(179):903–22.
[29] Tyczkowski J, Ledzion R. J Appl Phys 1999;86:4412–8.