Plasma polymerised thin films for flexible electronic applications

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ABSTRACT

The significant advancement and growth of organic and flexible electronic applications demand materials with enhanced properties. This paper reports the fabrication of a nonsynthetic polymer thin film using radio frequency plasma polymerisation of 3,7-dimethyl-1,6-octadien-3-ol. The fabricated optically transparent thin film exhibited refractive index of approximately 1.55 at 500 nm and rate of deposition was estimated to be 40 nm/min. The surface morphology and chemical properties of the thin films were also reported in this paper. The optical band gap of the material is around 2.8 eV. The force of adhesion and Young's modulus of the linalool polymer thin films were measured using force-displacement curves obtained from a scanning probe microscope. The friction coefficient of linalool polymer thin films was measured using the nanoscratch test. The calculated Young's modulus increased linearly with increase in input power while the friction coefficient decreased.

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1. Introduction

The past few years have seen a significant and rapid growth in research and development of organic thin film devices [1]. The advancement is especially noticeable in organic electronic systems such as flexible and large-area electronic displays, thin film transistors and thin film organic photovoltaic devices [2,3]. Many commercial organic devices are already in the market, typically organic light emitting diodes, organic field effect transistors (OFETs), organic solar cells, and polymer coated contact lenses or catheters [4,5]. One of the major driving forces behind the organic semiconductor research is the desire to replace inorganic materials, such as silicon and germanium, with lower fabrication cost and environmentally friendly alternatives [6]. Other significant advantages of organic semiconductors include the reduced number of physical defects compared to inorganic semiconductors, and ability to tailor material properties by choosing a precursor from a vast array of available volatile organics. This work focuses on the development of an insulating material, which can be incorporated in the OFET structure to make the flexible electronics a reality [7,8].

Surface modification of bulk materials using plasma enhanced technologies is an attractive method of imparting desirable surface properties onto the material while preserving its bulk characteristics [9,10]. Plasma polymerisation is broadly used for fabricating polymer thin films from volatile monomers [11,12]. A high degree of material diversity of the polymer thin films can be attained by changing the deposition parameters such as pressure, monomer flow, and input radio frequency (RF) power, to name a few [13–15]. As such, physico-chemical, mechanical, and surface properties, as well as the degradation behaviour of the plasma polymerised thin films can be tailored to suit a desired application [16]. Furthermore, the technique can be effectively employed for the polymerisation of organic compounds that may not undergo conventional thermo-chemical polymerisation [17].

The precursor 3,7-dimethyl-1,6-octadien-3-ol (linalool) is a naturally occurring terpene alcohol. Linalool is a key constituent of several essential oils, including lavender oil, basil, rosewood and coriander and is primarily used in fragrances and aromatherapy for its perfume and medicinal characteristics that include anti-stress, antibacterial and sedative properties [18–20]. This work investigates the feasibility of using plasma polymerisation to fabricate thin solid films from this naturally occurring compound without the need for additional processing. Research has previously been conducted to investigate properties of polymer thin films fabricated from eucalyptus and lavender oils [21–24] and components such as terpene-4-ol [8,14,25,26] and linalyl acetate [27,28].

2. Experimental details

2.1. Film fabrication

Polylinalool thin films were fabricated in accordance with the experimental procedure outlines elsewhere [29]. Typically the fabrication system consists of an RF plasma generator, a custom-made glass tube (*l* 70 cm, *d* 5 cm), a vacuum pump and vacuum gauges. We have fabricated the thin films at a pressure of 13 Pa, RF frequency of 13.56 MHz and at various RF power levels. For each deposition,

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1 ml of linalool was placed in the monomer flask. The monomer flow rate, F, was measured using a procedure outlined in previous studies by Gengenbach and Griesser [30]. The reactor chamber was first evacuated, then the monomer was released into the chamber. Once the pressure had stabilised, the vacuum valve was closed; the pressure was recorded every 5 s for 1 min. The flow rate F was calculated as $F = dp/dt \times 16172\ V/T$, where V is the volume of the chamber, T is the temperature, p is the pressure inside the reactor chamber and t is time. F was estimated to be 13.75 cm³/min during the polymerisation process.

2.2. Material characterisation

Optical constants and thickness of polylinalool thin films were estimated from ellipsometer parameters Ψ and Δ collected over the wavelength range of 190–1000 nm using a variable angle spectroscopic ellipsometer (J.A. Woollam Co., Inc., model M-2000D). Gaussian and Tauc–Lorentz oscillators were applied to both reflectance and transmission data to obtain the best fit to the experimental data. Direct and indirect optical band gap of polylinalool was calculated using the Tauc relation applied to the absorption data obtained using an Avantes AvaSpec 2048 UV–vis spectrometer. Tauc relation is described as $\alpha h\upsilon = B\ (h\upsilon - E_o)^p$, where α is the absorption, $h\upsilon$ is the energy of light, B is related to the length of localised state tails, E_o is the optical band gap and p is a constant that determines the type of transmission. For direct band gap, the Tauc relation is applied for $p = 1/2$, whereas for indirect band gap, $p = 2$ is used.

The surface morphology of the polylinalool thin films was investigated using the NT-MDT NTEGRA Prima atomic force microscope (AFM). A Hysitron Triboscope Nanomechanical unit in conjunction with the AFM system was used for nanoscratch test to determine the friction coefficient of the polylinalool material. Scratches were performed using a Berkovich tip, with a ramped load with the upper limit varied from 1000 nN to 2000 nN over 30 s. The cross hatch test using the Elcometer 107 kit was also performed to obtain a standardised (ASTM D3359) qualitative assessment of the adhesion between polylinalool films and glass substrate.

The Veeco TMX-2000 Explorer scanning probe microscope (SPM) was used in force-versus-distance mode (f–d mode) to generate force–displacement curves measuring the interactions between the tip and sample surface [31]. For each polylinalool sample, f–d curves were generated at 15 locations using a conical tip and a cantilever spring constant of 0.08 N/m. The adhesion force of the sample was calculated as $F_{ADH} = (SP + D_0 + D_A) \times k/m_s$, where F_{ADH} is the adhesive force, SP a set point, D_0 the zero level for the curve, D_A the adhesive deflection and m_s the gradient of the approach curve for silicon (in this case $m_s = 0.14$). Young's modulus was calculated as $F_{cone}\ (\sigma) = 2E^*\sigma^2\ /\ (\pi\ \tan\alpha)$, and $1/E^* \approx (1 - \mu^2)\ /\ E_{sample}$, where F_{cone} is the applied force of the conical tip, σ the indentation, E^* the relative Young's modulus, α the half angle of the tip (in this case, $\alpha = 11°$), E_{sample} the Young's modulus of the sample, and μ Poisson's ratio for the sample. Poisson's ratio of 0.35 is assumed for polylinalool thin films.

3. Results and discussion

3.1. Deposition rate and films thickness

The spectroscopic ellipsometry studies demonstrate that the polylinalool thin film thickness increases linearly with time and the rate of deposition was approximately 40 nm/min. With increase in input RF power, the rate of deposition decreased, which can be attributed to the higher degree of fragmentation of the monomer molecule. Therefore, films fabricated at higher input RF power were characterised by higher density and increased degree of cross-linking. Furthermore, the process of ablation may be more prominent in the case of high
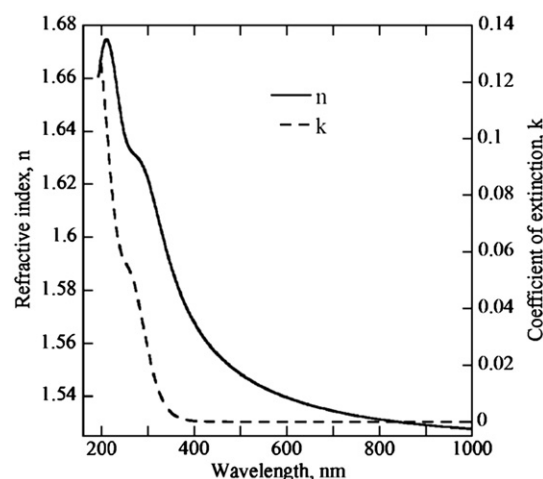

Fig. 1. Refractive index and extinction coefficient of polylinalool thin films deposited at 25 W.

power conditions, etching back the newly formed thin layer [15]. These results are in agreement with previously reported studies for similar compounds [21,22,29]. It is therefore possible to fabricate thin films of desired thickness to suit given application by controlling such deposition conditions as time and applied RF power.

3.2. Optical properties

Spectroscopic ellipsometry was used to measure the optical absorption of polylinalool thin films fabricated at different RF powers and estimate the refractive index, extinction coefficient and optical band gap. Fig. 1 shows the typical refractive index and extinction coefficient profiles for polylinalool thin film. The refractive index of polylinalool was slightly greater than that of the glass substrate, at 1.55 at 500 nm. Above 400 nm, the extinction coefficient was negligible, confirming that polylinalool is optically transparent. For films fabricated at 25 W under varied time, a deviation in measured optical parameters occurred over the lower wavelength region, with both indices increasing with thickness. However, the increase was insignificant. Similarly, there was no significant difference between optical profiles for the samples deposited at different RF power levels.

The effect of applied deposition power on the optical band gap E_o of polylinalool was investigated using UV–vis spectroscopy data. Thin films were manufactured for 10 min and their absorption profile data were obtained. Increase in the input RF power level had no significant effect on the general shape of the absorbance profiles, with all curves displaying a single peak at approximately 310 nm. The variance in height of the peak was attributed to the differences in film thickness.

The optical band gap E_o values are obtained from the UV–vis data using the Tauc relation and the results of films deposited at seven different power levels are summarised in Table 1. It was found that $p = 1/2$, which is commonly assumed for semiconducting plasma

Table 1
The influence of RF power on the refractive index and optical band gap of polylinalool thin films.

RF power level (W)	Thickness (nm)	Refractive index (at 500 nm)	Optical band gap (eV)
15	313.7	1.56	2.81
25	289.0	1.55	2.82
35	245.3	1.57	2.85
50	243.7	1.57	2.74
75	197.4	1.55	2.64

polymer thin films, also provided the best fit for polylinalool samples. The decrease in optical band gap of polylinalool with increase in applied power shows that it is feasible to tailor electrical and optical properties. A summary of refractive index, film thickness and band gap parameters is listed in Table 1.

3.3. Chemical properties

The FTIR spectra collected for the liquid linalool monomer and polylinalool thin films are presented in Fig. 2. The chemical structure of polylinalool was found to be notably different from that of linalool monomer, with a significant reduction in −OH moiety and complete dissociation of C=C unsaturation. A band corresponding to ketone, not present in the infrared spectrum of the monomer, was observed in spectra of all polylinalool films. It is likely that post-deposition ageing and associated oxygen uptake and radical termination would also contribute to the formation of moieties not present in the structure of the original polymer, as has been demonstrated previously [13,31,32]. The presence of strong methyl bands (~1465 cm^{-1}) and comparatively weaker methylene bands (~1375 cm^{-1}) indicated chain branching, commonly observed in plasma polymers, and implied that polylinalool film consists of a large quantity of short polymer chains.

3.4. Surface and mechanical properties

AFM images of the surface profiles collected for polylinalool films fabricated at 50 W is shown in Fig. 3. The images exhibit smooth, uniform and pinhole free surface with an average roughness of 0.44 nm. Closer examination of the surface reveals that although increasing RF power levels affected the surface topography with peaks becoming thinner and sharper compared to the surface profiles of films fabricated at lower RF power, this change was not significant. The root mean square (RMS) roughness was found to be independent of deposition power.

The friction coefficient was measured for polylinalool thin films fabricated at 25, 50 and 75 W using the nanoscratch test with the applied load ramping up to 1000 nN, 1500 nN and 2000 nN. Fig. 4 presents an AFM image of three scratch tests performed on the surface of 75 W sample, and the respective depth profile taken along the cross section plane (illustrated by white line). As expected,
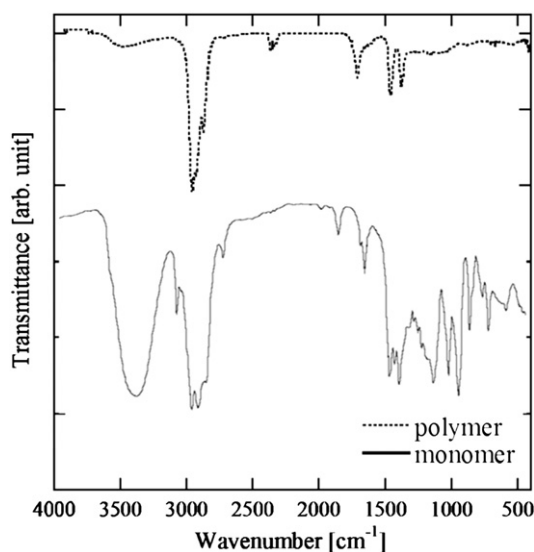

Fig. 3. AFM images of polylinalool thin films fabricated at 50 W.

the depth of the scratch increases for increasing applied load. A pile-up (indicated by the lighter shading) is due to the specific shape of the Berkovich tip used in the analysis.

Nanoscratch data for 2000 nN applied loading was used to determine the manner in which RF power affected the friction coefficient profiles for polylinalool films. The friction coefficient of the polylinalool thin films decreased for higher RF deposition powers. The Young's moduli were calculated from f–d curves collected for films deposited at varied RF power. To determine the value for the adhesive force, the generated f–d curves were averaged prior to surface adhesion calculation. For films fabricated at or above 15 W, there was a linear direct relationship between Young's modulus and RF power while surface adhesion remained approximately constant at 49 nN for all polylinalool samples independent of deposition power.

3.5. Substrate adhesion

The adhesion of polylinalool thin films to glass substrates was assessed qualitatively using the cross hatch test on samples manufactured

Fig. 2. FTIR spectra for the linalool monomer and the resultant polymer thin films fabricated using plasma polymerisation at 25 W RF power for 30 min.
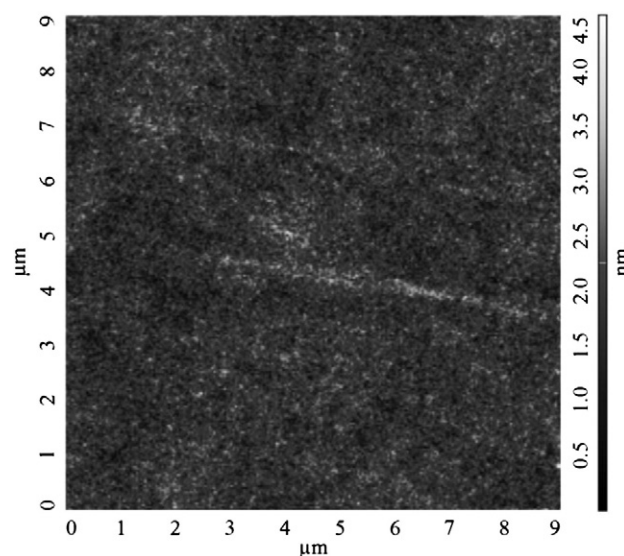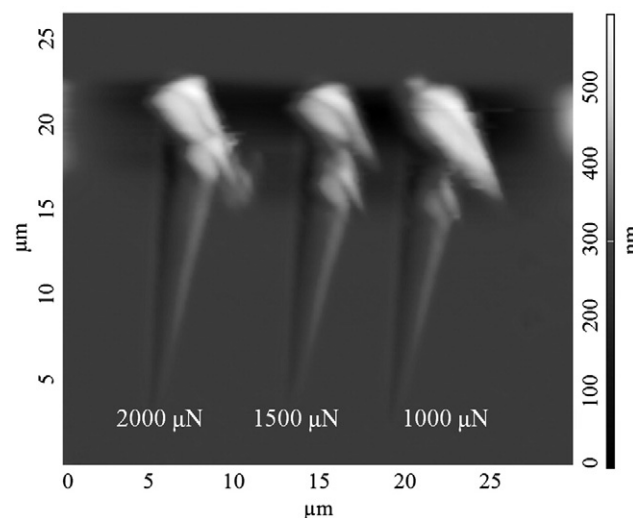

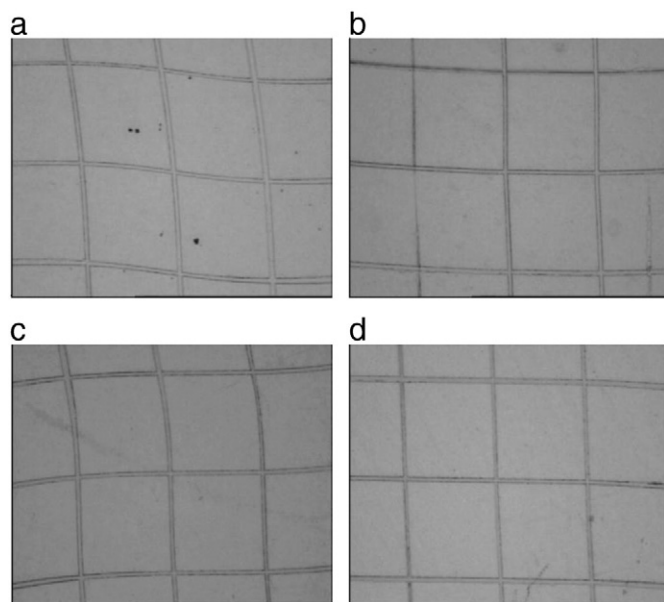**Fig. 4.** AFM image of the scratches performed on the polylinalool thin film deposited at 75 W.

Fig. 5. The qualitative analysis of the cross hatch test performed on samples deposited at a) 25 W, b) 35 W, c) 50 W, and d) 75 W.

at RF power levels of 5, 10, 15, 25, 35, 50 and 75 W. Images of the scratched film surfaces are presented in Fig. 5 and the classified adhesion values are listed in Table 2. Even though polymerisation below 15 W RF power is possible, good adhesion without delamination is obtained only above 15 W RF. For films deposited at power levels of above 15 W, there was little variation in the adhesion behaviour of the films. Better adhesion for films deposited at higher RF power is expected since increased energy input and subsequent ion bombardment can significantly enhance bonding between the substrate and the thin film.

4. Conclusion

RF plasma polymerisation was demonstrated to be an effective tool for polymerising linalool and fabricating linalool based polymer thin films. Deposition rate decreased linearly with RF power due to enhanced fragmentation of the monomer molecule and the more prominent process of ablation associated with high power conditions. AFM examination of the films demonstrated smooth, defect free surfaces, with roughness of approximately 0.44 nm for all samples independent of thickness and deposition power. Refractive index was found to be independent of RF power and thickness, ranging from 1.54 to 1.57 at 500 nm for all samples. The optical band gap decreased linearly from 2.81 for 15 W to 2.64 for 75 W samples. This recommends prospect of tailoring the polylinalool as a potential material for flexible electronic applications by means of suitable doping. Young's modulus and adhesion of polylinalool thin films to the substrate increased with deposition power, the increase attributed to higher degree of cross-linking within the bulk of the polymer and improved interfacial bonding. The surface adhesion of polylinalool films remained relatively constant for all samples.

Overall, RF plasma polymerisation of 3,7-dimethyl-1,6-octadien-3-ol is cheap and environmentally friendly processing and will be a potential candidate to employ as an organic polymer thin film in plastic electronics and as an encapsulation layer. In addition such layers can also be incorporated in other communication applications [33].

Acknowledgements

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Table 2
Substrate adhesion of polylinalool thin films as a function of RF deposition power.

RF power level (W)	Scratch 1	Scratch 2	Scratch 3
25	5B	4B	4B
35	5B	4B	5B
50	5B	5B	5B
75	5B	5B	5B