



Photocurable propyl-cinnamate-functionalized polyhedral oligomeric silsesquioxane as a gate dielectric for organic thin film transistors



Yuntae Kim^a, Jeongkyun Roh^b, Ji-Hoon Kim^a, Chan-mo Kang^b, In-Nam Kang^c, Byung Jun Jung^d, Changhee Lee^{b,*}, Do-Hoon Hwang^{a,*}

^a Department of Chemistry, and Chemistry Institute for Functional Materials, Pusan National University, Busan 609-735, Republic of Korea

^b School of Electrical Engineering and Computer Science, Inter-University Semiconductor Research Center (ISRC), Seoul National University, Seoul 151-744, Republic of Korea

^c Department of Chemistry, The Catholic University of Korea, Bucheon 420-743, Republic of Korea

^d Department of Materials Science and Engineering, The University of Seoul, Seoul 130-743, Republic of Korea

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ABSTRACT

A polyhedral oligomeric silsesquioxane (POSS)-based insulating material with photocurable propyl-cinnamate groups (POSS-CYNNAM) was designed and synthesized through simple single step reaction for use as a gate dielectric in organic thin-film transistors (OTFT). POSS-CYNNAM was soluble in common organic solvents and formed a smooth thin film after spin-casting. A thin film of POSS-CYNNAM was cross-linked and completely solidified under UV irradiation without the use of additives such as photoacid generators or photoradical initiators. ITO/insulator/Au devices were fabricated and characterized to measure the dielectric properties of POSS-CYNNAM thin films, such as leakage current and capacitance. A pentacene-based OTFT using the synthesized insulator as the gate dielectric layer was fabricated on the transparent indium tin oxide (ITO) electrode, and its performance was compared to OTFTs using thermally cross-linked poly(vinyl phenol) (PVP) as the insulator. The fabricated POSS-CYNNAM OTFT showed a comparable performance to devices based on the PVP insulator with $0.1 \text{ cm}^2/\text{Vs}$ of the field effect mobility and 4.2×10^5 of an on/off ratio.

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1. Introduction

Intensive research on solution-processable organic thin film transistors (OTFTs) has resulted in low-cost, flexible and foldable electronic devices through the use of diverse printing technologies. Many efforts have been directed towards increasing the mobility of OTFTs to the level observed for amorphous silicon transistors. As a result, in the near future, OTFTs can be expected to be employed in the backplane of organic light-emitting diode displays, e-papers, smart cards and radio frequency identification

tags [1–3]. In the early stages of development, OTFTs performed relatively poor, but they have been remarkably improved in recent years by the development of high-mobility organic semiconductors, insulators, as well as by improving the interface contacts. As a result, the mobility of pentacene OTFTs has reached $5 \text{ cm}^2/\text{Vs}$ [4], while those based on solution-processable polymers or oligomers have reached $2.5 \text{ cm}^2/\text{Vs}$, which is higher than mobilities observed for amorphous silicon TFTs [5].

To fabricate low-cost high-performance OTFTs, insulators are required that are solution-processable and that can be used in various printing techniques, while they should also have good insulating and pattern-forming properties. So far, inorganic insulators such as Al_2O_3 , HfO_2 , and SiO_2 have been used in high-performance OTFTs.

* Corresponding authors. Tel.: +82 51 510 2232.

E-mail addresses: chlee7@snu.ac.kr (C. Lee), dohoonhwang@pusan.ac.kr (D.-H. Hwang).

For the fabrication of larger devices by cost-effective solution processes, many polymer thin films based on poly(vinyl phenol) (PVP), poly(methyl methacrylate), poly(vinyl alcohol), polystyrene, silsesquioxane polymers, CYTOP, and polyimide (PI), and polyhydrazide have been researched and reported to function as the insulator in OTFTs [6–12]. Some polymer insulators such as polyimide and PVP require high temperature thermal annealing at temperatures to get high quality thin films that in some cases may reach temperatures as high as 200–250 °C [6,11], which is incompatible with flexible and plastic electronics. Ideally, for low-cost high-performance OTFTs, high quality solution-processable insulators need to be developed that allow low temperature processing. Here, the photocuring process is a promising candidate because the process temperature can be adapted to the use of plastic substrates. Despite this favorable characteristic, only a few studies have focused on developing high quality photocurable polymer insulators. Photo-patternable polyimides were reported by Pyo and his coworkers as a low temperature processable gate dielectric layers for OTFTs, but the processing temperature (~160 °C) was still high for employing plastic substrate [13,14]. A photo-curable insulating layer composed of poly(vinylphenol), 1,2,4,5-tetraacetoxymethylbenzene, and 2,4-bis(trichloromethyl)-6-aryl-1,3,5-triazine was also reported by Jang et al as a gate dielectric for OTFTs [15]. In this paper, however, a photo-acid generator was needed for photo-curing and also octadecyltrichlorosilane was used after plasma treatment to remove remaining hydroxyl groups. Poly(acrylates) with various functional groups were also used as photo-curable insulators for OTFTs by Su et al. [16,17]. The poly(acrylate) insulators showed good performances but they needed a photo-radical initiator for photo-curing, and also the device performances were somewhat sensitive to the post treatment conditions.

We recently reported the synthesis of polyhedral oligomeric silsesquioxane (POSS) derivatives containing photocurable epoxy functional groups as a new class of photopatternable organic/inorganic hybrid materials [18]. POSS has a cubic structure and can contain eight functional groups at each cube corner [19–21]. It has good thermal stability, as well as a high water- and corrosion-resistance, and is a good electrical insulator. Our previous POSS derivative with the epoxy functional groups, however, needed a photo-acid generator for photocuring, which could be potential charge trap sites. In this study, we introduced photocurable propyl-cinnamate groups at the eight cube corners (Scheme 1). Under UV-light irradiation the cinnamate group forms a 4-membered cyclic structure by a [2 + 2]-cyclization reaction [22], which allows the POSS-CYNNAM to be polymerized and solidified below 120 °C using solely UV irradiation without any photo-acid generators or photo-radical initiators. We fabricated a metal/insulator/metal (MIM) device to evaluate the electrical properties of the cross-linked POSS-CYNNAM thin film, and also prepared and characterized pentacene OTFTs with POSS-CYNNAM as the gate dielectric. The performance of POSS-CYNNAM OTFTs was compared with OTFTs fabricated using thermally cross-linked PVP as the insulator.

2. Results and discussion

Allyl cinnamate was synthesized by the reaction of cinnamoyl chloride and allyl alcohol (Scheme), after which the allyl cinnamate was introduced onto the eight cube corners of POSS by a hydrosilylation reaction using Pt/C as a catalyst. The successful synthesis of POSS-CYNNAM was confirmed by the corresponding ¹H- and ¹³C-NMR spectra (Fig. 1a and b, respectively). After the hydrosilylation reaction, the characteristic resonances of the allyl protons of the allyl cinnamate at 5.85 (*H_f*), 5.37 (*H_g*), and 5.27 (*H_h*) ppm had disappeared completely, while the protons of the double bond in POSS-CYNNAM were observed as two doublets at 7.68 (*H_a*) and 6.44 (*H_d*) ppm, respectively. New signals appeared after the hydrosilylation reaction that corresponded to the alkoxymethylene protons (*H_f*, 4.13 ppm), the protons at the β-silyl methyl carbon (*H_g*, 1.71 ppm), the α-silyl methylene carbon (*H_i*, 0.61 ppm), and the α-silyl methyl carbon (*H_j*, 0.15 ppm). In the POSS-CYNNAM ¹³C-NMR spectrum, three signals appeared that corresponded to the carbonyl carbon (*C_a*, 167.1 ppm), and the two vinyl carbons (*C_b* and *C_c*, 144.8, 118.4 ppm, respectively), whereas the alkoxy carbon (*C_h*), β-silyl methylene carbon (*C_i*), α-silyl methylene carbon (*C_j*), and α-silyl methyl carbon (*C_k*) were visible at 67.1, 22.6, 13.8, and –0.1 ppm, respectively.

The UV-vis absorption of the 60 nm-thick POSS-CYNNAM solid film was studied versus the UV irradiation time at 80 °C as shown in Fig. 2. Whereas POSS has no characteristic absorption in the UV-vis, POSS-CYNNAM showed a strong absorption around 275 nm resulting from the π–π* transition of the cinnamate group. The intensity of the absorption at 275 nm decreased gradually with an increase in UV irradiation time. This can be attributed to the consumption of the cinnamate double bonds by the occurrence of the UV-induced [2 + 2] cyclo-addition reaction [22]. The absorption peak of the carbonyl group of POSS-CYNNAM almost completely disappeared after UV irradiation for 360 s.

The change in FT-IR spectra of the POSS and POSS-CYNNAM thin films was also studied at different UV irradiation times (Fig. 3). POSS-CYNNAM was mixed with KBr, and fabricated to a pallet form for FT-IR measurement. Thickness of the KBr pallet was much thicker than the film for UV measurement, so longer time was needed for the UV curing. For the POSS film, a strong absorption of the Si–H bond was observed at 2144 cm⁻¹, as well as the absorption of the C–H stretching vibration of the α-silyl methyl group at 2900–3000 cm⁻¹. In the FT-IR spectrum of POSS-CYNNAM, the C–H stretching vibration of the phenyl ring and the alkene appeared at 2900–3100 cm⁻¹. The characteristic peak at 2144 cm⁻¹ corresponding to the Si–H stretching vibration had disappeared in the spectrum of POSS-CYNNAM. The characteristic absorption of the α,β unsaturated carbonyl group, and that of the vinyl group were observed at 1716 and 1637 cm⁻¹, respectively. The peak intensity and absorption position of the carbonyl and vinyl groups in POSS-CYNNAM changed upon UV irradiation as a result of the [2 + 2] cyclo-addition reaction, while also the peak position of the carbonyl group changed

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