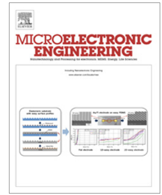
Microelectronic Engineering 118 (2014) 6–10

Contents lists available at ScienceDirect

Microelectronic Engineering

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



Electrical characterizations of solution-processed dielectric layer of octamethylcyclotetrasiloxane

Hunsang Jung [a], Minkeun Kim [a], Yejin Kim [a], Sewook Oh [a], Chi-Jung Kang [b], Tae-Sik Yoon [c], Hyun Ho Lee [a,*]

[a] Department of Chemical Engineering, Myongji University, Gyeonggi 449-728, Republic of Korea
[b] Department of Physics, Myongji University, Gyeonggi 449-728, Republic of Korea
[c] Department of Material Science and Engineering, Myongji University, Gyeonggi 449-728, Republic of Korea

ARTICLE INFO

Article history:
Received 15 April 2013
Received in revised form 3 January 2014
Accepted 7 January 2014
Available online 18 January 2014

Keywords:
Octamethylcyclotetrasiloxane
Solution process
MIS capacitor
ZTO
TFTs

ABSTRACT

Solution processed dielectric layer was fabricated with octamethylcyclotetrasiloxane (OMTS) by UV/ozone oxidation and thermal annealing. Annealing temperatures of 100 °C, 300 °C, and 500 °C were examined and their dielectric properties were characterized on structures of metal–insulator–silicon (MIS) capacitor and thin film transistor (TFT) with solution-processed zinc-tin-oxide (ZTO) semiconductor. Chemical changes from the UV/ozone oxidation and annealing were analyzed by FTIR and XPS. For the 500 °C annealed dielectric layer with UV/ozone oxidation, no hysteresis in capacitance–voltage (*C*–*V*) measurement was detected having a high dielectric constant (*k*) of 5.52. The OMTS film can be applicable as a gate dielectric layer towards intensive development of printed electronics.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Solution process using liquid precursors for electronic materials has been attracting considerable attentions in pursuit of drastic development of printed electronics [1–16]. In addition, along with tremendous progress of direct patterning methods, which can replace conventional photolithography, the researches for the soluble precursor have been continuously highlighted [1–8,10–16]. However, while the intensive advances have been reported and accomplished for semiconductor precursors, there have been relatively limited numbers of focuses on the soluble dielectric layers, especially with inorganic materials [1–8]. Actually, most of soluble gate dielectrics have been organic polymers, such as polymethylmethacrylate (PMMA), polyvinylphenol (PVP), polyvinylalcohol (PVA), parylene, polyimide (PI) and so on [1,2]. Moreover, the polymeric dielectric layers were compatible with organic semiconductor materials, which have leaded bendable or flexible electronics [3].

Table 1 shows soluble dielectric reports using silane or siloxane-based liquid precursors. Silsesquioxane resin as an organic/inorganic hybrid and low molecular weight oligomeric precursor was reported to be adopted for a high performance gate dielectric polymer on flexible substrate [1]. Additionally, as shown in Table 1, sol–gel formation methods have been mainly used for the formation of silane or siloxane-based dielectric films [2,4–11]. For example, hexamethyldisilazane (HMDS), methyltriethoxysilane (MTOS), methacryloxypropyl trimethoxysilane (MPTMS), diphenylsilanediol (DPSD), vinyltrimethoxysilane (VTMS), mercaptopropyltrimethoxysilane (MPTMS), and tetraethoxysilane (TEOS) were hydrolyzed by reacting with water and ethanol to form silicate or silicon oxide [4–11]. The hydrolysis reaction was accelerated by acid catalyst or HCl, and then, the liquid silane and siloxane precursors undergo condensation and polymerization by base catalyst such as NH_4OH and $Ba(OH)_2$ [6–8,11]. However, the acid and base catalyst for the sol–gel method can be sources of mobile ions inside of resultant dielectric layers, which can invoke flatband voltage shift (ΔV_{FB}) or threshold voltage shift (ΔV_{th}) in the device formats of MIS capacitor and TFT.

The silicates formed by sol–gel methods were frequently surface-modified by trimethylchlorosilicate (TMCS) to cover Si–OH groups on the porous surface. It was developed as a low *k* material to reduce interconnects delay of passivation layer in the microelectronics [3,6]. The hydroxyl group and moisture also influenced polarizability and threshold voltage shift. When the TEOS and HCl were used for formation of sol–gel silica layer with pentacene semiconductor, the TFT showed significantly detectable hysteresis in I_d–V_g curves, where silanol groups (Si–OH) inside the modified sol–gel dielectric were considered as deep trap source for electron [4–6]. Therefore, removal of Si–OH groups inside of inorganic silicate or siloxane dielectric films is critical to be an adequate dielectric layer.

* Corresponding author. Tel.: +82 31 330 6381; fax: +82 31 337 1920.
E-mail address: hyunho@mju.ac.kr (H.H. Lee).

0167-9317/$ - see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.mee.2014.01.004

Table 1
A comparison table for silane or siloxane-based soluble dielectric layers.

Silicon based soluble precursor (catalyst)	Annealing or curing temperature (photo-curing)	Active channel (semiconductor)	Mobility	Breakdown voltage (MV/cm)	Threshold voltage (V_{th}: V)	Refs.
Silsesquioxane polymer	135 (none)	FCuPc, CuPc, P3HT, α-6T, DH-α-5T, pentacene	0.003, 0.0026, 0.02, 0.006, 0.045, 0.1	–	–	[1]
HMDS (acid)	450 (none)	–	–	>1.0	–	[2]
MTOS, TEOS (acid)	190 (none)	DH4T	0.005	1.4–1.65	−0.3	[4,5]
TEOS (HCl, NH_4OH)	100 (none)	Pentacene	0.67, 1.43, 2.08	–	−0.23	[6,7]
MPTMS, DPSD ($Ba(OH)_2$)	100 (none)	P3HT	0.0046	>1.0	5.0	[8]
SOG (polysilsesquioxane)	150 (none)	Soluble ZnO	1.2	>0.5	10	[10]
VTMS, DPSD, MPTMS ($Ba(OH)_2$)	150 (UV)	Pentacene	0.113	>1.0	–	[11]
POSS	120 (UV)	Pentacene	0.18	>1.0	−28	[12]

FCuPc, hexadecafluoro copper phthalocyanine; CuPc, copper phthalocyanine; P3HT, poly(3-hexylthiophene); DH-α-5T, dihexyl-α-5T; HMDS, hexamethyldisilazane; DH4T, α,ω-dihexylquaterthiophene; MTOS, methyltriethoxysilane; TEOS, tetraethylorthosilicate; MPTMS, methacryloxypropyl trimethoxysilane; DPSD, diphenylsilanediol; VTMS, vinyltrimethoxysilane; MPTMS, mercaptopropyltrimethoxysilane; POSS, polyhedral oligomeric silsesquioxane.

However, the TEOS or modified silicate(ormosil) hybrid of MTOS have provided new opportunities for preparing smart organic/inorganic hybrid materials at a relatively low temperature around 100 °C, despite of limitations as inorganic brittle material [4,5].

Advances of silane and siloxane-based dielectric layers have been more progressed with photo-treatment or photo-induction of siloxane-based precursor such as silsesquioxanes [9]. In addition, with introduction of soluble inorganic (*i.e.* metal-oxide) semiconductor process, more studies about the soluble dielectric precursors have been reported [10]. The photo-induced or photo-curable precursors have been evolved into more sophisticated reactions like thiol-ene and cinnamate cross-linkings [11,12].

Very recently, many reports about forming efficient soluble dielectric layers using polymers with cross-linkers like trichlorosilyl reagents [3,13,14], and metal oxides such as HfO_x and ZrO_x [15,16]. The cross-linked dielectric polymers could be formed ultrathin even at low temperature [3,13] and the metal oxide dielectrics could show their expected high k performances [15,16]. However, the cross-linked organic polymer layers had been mainly demonstrated and optimized for organic semiconductor layers of pentacene or semiconducting polymers such as poly(9,9-dioctylfuorene-co-bithiophene) (F8T2) or poly(3-hexylthiophene) (P3HT). In addition, the dielectric layers made of metal oxides necessitated air or moisture-sensitive precursor, which required an extensive care to perform depositing or filming process [15]. Furthermore, the dielectric films made of metal oxides should be sustained in amorphous state to keep high k performance, which could limit any additional thermal treatment [15,16].

Octamethylcyclotetrasiloxane (OMTS), $[(CH_3)_2SiO]_4$, which is known as D_4, is a cyclic monomer or oligomer for polymerization of polydimethylsiloxane (PDMS), which is one of polysiloxanes ($[-SiO_2(R)_2-]_n$) [17,18]. For the purpose of electronic material formation, the OMTS has been introduced as precursor for plasma enhanced chemical vapor deposition (PECVD) or hot filament chemical vapor deposition (HFCVD) processes to have amorphous silicon oxide layer [17,18]. The OMTS has advantage over the TEOS in low carbon abundance or content as the precursor for the PECVD and HFCVD. However, the PECVD process could result in aging effects of traps from free radicals or dangling bonds and brittle or inflexible films upon exposure to the atmosphere [17]. In addition, low k characteristics from the OMTS precursor had blocked further intensive trials for gate dielectric applications [17,18].

Recently, a photochemical conversion of the PDMS by strong UV irradiation and ozone formation was reported to be effective to fabricate dielectric layer [19]. The key issue of photochemical conversion of the PDMS was to reduce the carbon abundance in the film. Atomic ratio concentration of O:Si could be changed from 1:1 (PDMS) to 2:1 (SiO_2) for the evidence of migration of the bulk PDMS to the new SiO_2 layer [19]. However, high energy UV (172 nm) irradiation from excimer lamp was required to form the efficient film and its thickness control was hindered by viscous and elastic nature of the PDMS.

In this study, the silane or siloxane-based OMTS, which is the oligomeric precursor of the PDMS polymer, was used as a soluble precursor to form electrical dielectric layer through UV/ozone oxidation and annealing at 100 °C, 300 °C, and 500 °C. Since it was not based on the sol–gel formation mechanisms, no acid and base chemicals were required. It was based on the photo-curable or photochemical process with UV–ozone treatment and designed for soluble inorganic semiconductor layer. The soluble dielectric layers were applied and examined in the structures of metal–insulator–silicon (MIS) capacitor and thin film transistor (TFT) compatible with soluble semiconductor precursor of zinc-tin-oxide (ZTO) [16,17]. The device characteristics were analyzed in terms of the performance of the OMTS dielectric layers.

2. Materials and Methods

Heavily boron doped p-type (1 0 0) silicon wafer with a resistivity of 10–15 Ω-cm was used as substrate both for fabrication of MIS capacitor and TFT. After native oxide was removed with diluted HF, the wafer was cleaned in acetone, isopropyl alcohol, and methanol. Precursor solution of OMTS (Sigma–Aldrich) without any further purification for the formation of dielectric film was spin-coated on the silicon wafer. Then, the spin-coated dielectric layers were UV/ozone treated for 1 h and annealed at 100 °C, 300 °C, and 500 °C in ambient condition, respectively. The source of UV/ozone treatment or oxidation was irradiated at 254 nm with low pressure mercury lamp in a UV/ozone cleaner (UVO-30, Jaesung Eng. Co.).

For measurement of refractive indexes of the OMTS films, an ellipsometer (Elli-SE, Ellipso Tech.) was used. Thickness of the OMTS was analyzed by scanning electron microscopy (SEM; Hitachi S-4300SE) and confirmed by measurement of surface profiler (Alpha step 500, KLA Tencor) and the ellipsometer. For MIS capacitor, 150 nm thick gold layers were evaporated to form a top electrode for MIS capacitor. The shape of the electrode measured by microscope was a circular dot of 0.75 mm in diameter. The capacitance–voltage measurement was carried out on the MIS capacitor with a LCR meter (Agilent 4284A) at 1 MHz.

For TFT device, precursor solution for the ZTO semiconductor film was prepared by dissolving zinc acetate dehydrate and tin acetate (Alfa Aeser) in ethylene glycol. The heavily boron-doped silicon substrate was served as common gate for the TFT device. The

Download English Version:

https://daneshyari.com/en/article/6943626

Download Persian Version:

https://daneshyari.com/article/6943626

Daneshyari.com