Pulsed plasma polymerized dichlorotetramethyldisiloxane high-*k* gate dielectrics for polymer field-effect transistors

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Polymerized dichlorotetramethyldisiloxane (DCTMDS) films deposited by radio-frequency pulsed plasma polymerization (PPP) demonstrated very high dielectric constants for a polymer-based system, in the range of 7–10. The high dielectric constants of PPP DCTMDS films are due to the high polarizability of the DCTMDS monomer. The pulsed plasma duty cycle (on/off) resulted in slightly higher dielectric constant DCTMDS films for higher duty cycles. The variation of dielectric constants does not show any trend with varying film thicknesses, indicating that the thickness of the deposited films is not significant for controlling permittivity. Postdeposition annealing in a certain temperature range improves the electrical integrity of PPP DCTMDS films, but temperatures that are too high induce even higher leakage than the samples with no heat treatment. An optimal annealing temperature was identified to be in the range of 150–200 °C. Samples annealed within this temperature window have low leakage current densities below 0.1 pA/μm^2 at 10 V for film thicknesses about 100 nm. Poly(3-hexythiophene) polymer field-effect transistors (PFETs) using PPP DCTMDS gate dielectric films were fabricated and tested. Due to the high dielectric constants of PPP DCTMDS, these PFETs possess high gate capacitance and operate at low voltage. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2150248]

High-*k* gate dielectrics are highly desirable for any metal-insulator-semiconductor field-effect transistors (MISFETs) as the capacitance of the gate insulator scales with permittivity, which is in turn proportional to the field-effect transistors' (FETs) output current. High dielectric constants of the gate insulator can elevate the output current and increase the electrical equivalent thickness of the insulator, which is important for scaled complementary metal-oxide semiconductor (CMOS). However, for polymer field-effect transistors (PFETs), an additional criterion is often required beyond inorganic FETs, which is a flexible dielectric. Flexibility is one key advantage for PFETs for niche applications. Thus, a suitable polymer dielectric that is flexible with high permittivity concurrently with low leakage current is needed.

The magnitude of the dielectric constant depends on polarizability of the insulator and the number of molecules per unit volume. Polarizability is the ability of the polarizable units, namely, electronic, atomic, and dipolar, in a polymer to orient quickly enough in response to the oscillations of an alternating electric field. A higher dielectric constant is demonstrated by polymers with high polarizability. The exact prediction of molecular polarizability involves tedious calculations. However, a simple estimation of polarizability is to sum tabulated polarizabilities of the molecule under consideration.[1–5] This method is used in our work to estimate the molecular polarizability of monomers and select a suitable monomer candidate.

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Plasma polymerization has the advantage of a wide selection of monomers;[6,7] thus, this work screened monomers containing atoms of high polarizability. The monomer dichlorotetramethyldisiloxane (DCTMDS) was selected for this study, which contains a –Cl functional group in its structure. DCTMDS has a high tabulated polarizability and therefore should greatly improve the dielectric constant of the polymer insulator over previous reports.[8]

This study of pulsed plasma polymerization (PPP) DCTMDS dielectric films was divided into three parts. Part one examined how the duty cycle affects the permittivity of polymerized DCTMDS dielectric films. Two duty cycles, 10 ms/90 ms and 10 ms/30 ms, were used to deposit DCTMDS dielectric films. For each duty cycle, two deposition durations were used to generate one thin sample and one thick sample. Therefore, this also tested if the permittivity shifts with film thickness. The deposition parameters and testing results are listed in Table I. The setup for radio-frequency pulsed plasma deposition was introduced previously.[8]

TABLE I. The effect of duty cycle and thickness on the dielectric constant of PPP DCTMDS films.

	Duty cycle	Deposition time (min)	Thickness (Å)	Relative dielectric constant
DCTMDSI1	10/90	12	600	7.3±0.15
DCTMDSI2	10/90	24	1300	9.2±0.24
DCTMDSI3	10/30	22	790	10.4±0.32
DCTMDSI4	10/30	37	1450	10.5±0.73

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TABLE II. The effect of postdeposition annealing on the properties of PPP DCTMDS dielectric films.

	Annealing temperature (°C)	Thickness (Å)	Relative dielectric constant	Leakage current density (pA/μm^2)
DCTMDSII1	N/A	1130	8.8±0.11	0.05
DCTMDSII2	150	1140	8.1±0.52	0.02
DCTMDSII3	200	1050	7.4±0.15	0.01
DCTMDSII4	250	1010	8.7±0.05	0.05
DCTMDSII5	300	860	4.9±0.13	1.5
DCTMDSII6	350	800	6.1±0.11	1.6

The film permittivity was evaluated by calculating the relative dielectric constant from the capacitance-voltage characteristics of the Au/PPP DCTMDS/Si MIS structures. All the relative dielectric constants are derived using *C-V* characteristics at a 1 MHz frequency. Five measurements were taken on each sample to check the consistency of the test results. The *C-V* characterization used an Agilent 4284A *LCR* meter coupled with Material Development Corporation CSM/WIN analysis software. The results listed in Tables I and II are the averages and standard deviations calculated from the five measurements for each sample.

Part two of this study identified the optimal temperature window for postdeposition annealing to reduce the leakage current through the dielectric. Six samples were prepared for this study. One of the six samples did not receive postdeposition annealing and was kept as the experimental control. The other five samples were annealed for 3 h in air at 150, 200, 250, 300, and 350 °C, respectively.

The third part of this study used the best quality PPP DCTMDS film as the gate dielectric for a bottom contact (coplanar) regioregular poly(3-hexylthiophene) (P3HT) PFETs. The thickness of the gate dielectric was about 850 Å, and it was annealed at 200 °C for 3 h. The gate was a boron-doped Si substrate with a resistivity of 0.05–0.1 Ω cm. The source and drain contacts are 0.5×0.5 mm^2 Au pads made by shadow mask evaporation. P3HT was applied in solution by spin coating. The P3HT PFETs were tested in a nitrogen atmosphere using Alessi probes and a Keithley 4200 semiconductor parameter analyzer.

The relative dielectric constants listed in Table I are calculated from the capacitance data using the equation

$$k_i = \frac{Ct}{\varepsilon_0 A}, \quad (1)$$

where C is the accumulative capacitance, t is the thickness of the PPP DCTMDS film, ε_0 is vacuum permittivity, and A is the area of the capacitor. The calculated relative dielectric constants are in the range of 7–10, which is significantly high for polymers that generally range between 2 and 4. The most commonly used polymers, such as polyethylene and Teflon, have dielectric constants of only a little higher than 2. The few reports of flexible polymer dielectric films used as gate insulators in PFETs,[9–13] such as polyvinylphenol or polyimide, generally have dielectric constants ranging from 3 to 3.5,

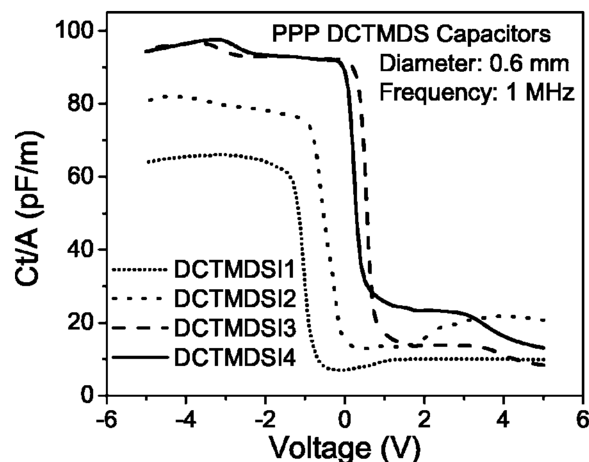

FIG. 1. Capacitance-voltage characteristics of MIS capacitors using PPP DCTMDS dielectric films at 1 MHz.

compared to the more common choice for PFETs of rigid SiO_2 which has a dielectric constant of 3.9.

The capacitance of samples DCTMDSI1 through DCTMDSI4 were normalized by area and thickness by A/t and plotted against gate voltage, as shown in Fig. 1. With the vertical axis being Ct/A in Fig. 1, the data in the accumulation region actually are representatives of the relative dielectric constant of the polymerized DCTMDS films. The effects of the duty cycle and thickness are listed in Table I, which shows that high duty cycles generate samples with slightly higher relative dielectric constants. For low duty cycle samples, thicker samples have higher relative dielectric constants, however, this phenomenon did not happen with high duty cycle samples. Therefore it seems that the thickness of the deposited films is not significant for controlling permittivity.

One problem identified with the as-deposited samples DCTMDSI1 to DCTMDSI4 is that they exhibit a leakage current density that is larger than generally acceptable for PFET operation. To address this problem, postdeposition annealing was employed, that was effective in earlier studies.[8] Annealing improves the material integrity and densifies the film. A set of six samples was prepared for the annealing study. Since the 10 ms/30 ms duty cycle was identified as producing a higher permittivity than a 10 ms/90 ms duty cycle according to the results of DCTMDSI1 through DCTMDSI4, the duty cycle of 10 ms/30 ms was selected for this annealing study. The annealing temperatures and testing results are listed in Table II. It is clear that all the annealed samples have lower relative dielectric constants than the as-deposited samples.

The thickness of the samples DCTMDSII1 through DCTMDSII6 before annealing was about 1150 Å. Sample DCTMDSII2 retained its thickness after annealing, but the rest of the samples became thinner due to the postdeposition heat treatment and higher annealing temperatures reduce the thickness more substantially.

Figure 2 shows that DCTMDSII2 and DCTMDSII3 have the best performance from the second series. The leakage current density of these samples is at least an order of magnitude smaller than the as-deposited sample. But, if the an-

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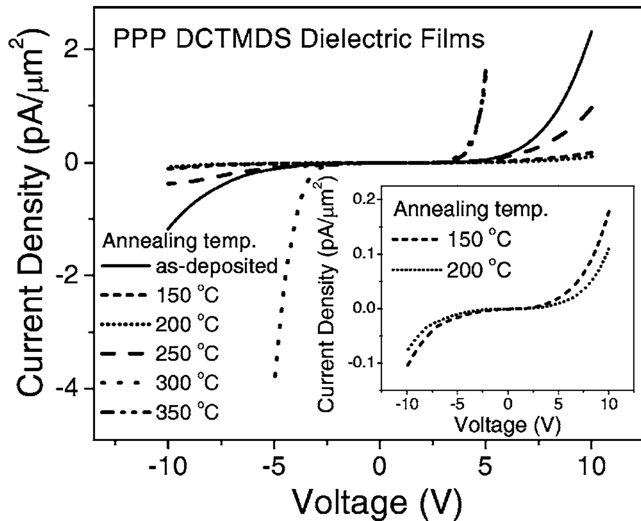
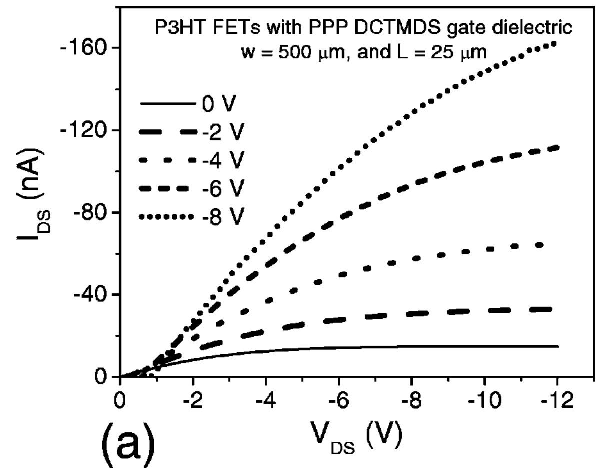


FIG. 2. Leakage current density of PPP DCTMDS dielectric films.

nealing temperature is too high, the samples will exhibit an even higher leakage than the unannealed DCTMDSII1. The best annealing temperature observed for polymerized DCTMDS is in the range of 150–200 °C. When the annealing temperature is less than or equal to 200 °C, the leakage current is reduced with increasing temperature due to the volatilization of undesired low molecular weight oligomers. However, once the annealing temperature surpasses 250 °C, the leakage current rises sharply. The samples annealed at the highest temperatures, DCTMDSII5 and DCTMDSII6, are damaged due to the breakage of relatively weak chemical bonds in the polymer, which contribute to film shrinkage and mobile ions.

Hysteresis, due to mobile charge or charge trapping/detrapping in or near the PPP DCTMDS dielectric film, was also examined and manifests as a shift in the flatband voltage, depending upon scan direction. For the as-deposited sample DCTMDSII1, its flatband voltage shifts upwards by 1 V when swept up in voltage initially followed by a reverse voltage sweep. The DCTMDSII3 sample, which had the lowest leakage current density, in contrast shifted downwards by 0.8 V. The downward shift of flatband voltage indicates that positively charged mobile ions in the PPP DCTMDS films account for the hysteresis in sample DCTMDSII3, whereas an upward shift of the flatband voltage in the as-grown sample (DCTMDSII1) is caused by negative charges injected into the dielectric film through the electrodes.

The electrical characteristics of P3HT PFETs substituting a PPP DCTMDS film as their gate dielectric are shown in Fig. 3. Compared to reports of PFETs in the literature,[14–19] the PFETs in this study operate at relatively low supply voltages because of the high PPP DCTMDS capacitance attributed to the high relative dielectric constant. The threshold voltage extrapolated from $I_{DS}^{1/2}$ vs V_G plot is about 3 V. With such a low threshold voltage, the PFETs with PPP DCTMDS achieve saturation at low V_{DS}. As expected, more negative gate bias accumulates more charges to the channel, so the transconductance of these PFETs increases with more negative gate bias. The subthreshold swing was ~6 V/decade and the subthreshold current was 1.6 nA or 3.2 nA/mm gate



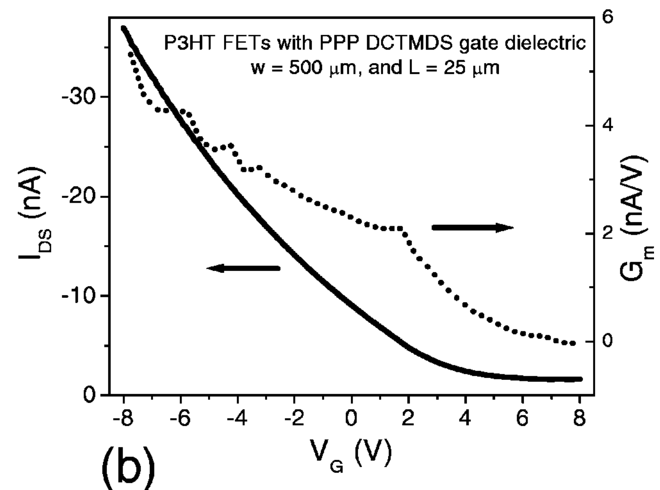


FIG. 3. Electric characteristics of P3HT PFETs using PPP DCTMDS gate dielectric. (a) I_{DS}-V_{DS} characteristics. (b) I_{DS}-V_G characteristics and extracted transconductance.

width. The relatively high leakage current in these PPP DCTMDS films limited the subthreshold characteristics. Subsequent experiments, not shown here, using a slow growth deposition "seed" layer have significantly reduced the leakage current by three orders of magnitude.

Finally, it was shown that the PPP DCTMDS films are resistant to immersion in typical chemical solvents, such as acetone, methanol, and isopropanol. They are even robust enough to withstand conventional photolithographic processing with no observable film shrinkage, warping, or peeling. Since working P3HT FETs on PPP DCTMDS films were demonstrated, it at least indicates that the films are also resistant to xylene, one of the most widely used solvents for electroactive polymers. Film adhesion was excellent and withstood the Scotch tape test. Therefore, with its functionality demonstrated in P3HT FETs and robustness examined in chemical and mechanical tests, it is evident that PPP DCTMDS is a promising insulator for flexible polymer circuits.

In conclusion, it was proven that polymerized DCTMDS has a high relative dielectric constant (about 7–10), due to the high polarizability functional group –Cl in its structure, as predicted by the Clausius-Mossotti relation. It was also

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observed that postdeposition annealing was an effective way to improve the performance of PPP DCTMDS dielectric films by reducing their leakage current. The annealing temperature in the range of 150–200 °C is optimum to limit leakage current within DCTMDS dielectric films. Annealing temperatures higher than 250 °C tend to overheat the samples and elevate the leakage current. High permittivity PPP DCTMDS gate dielectric provides high gate capacitance, so the P3HT PFETs operate at relatively low supply voltages.

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