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PTFE Nanoemulsions as Ultralow-k Dielectric Materials

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Summary: Modern integrated circuits require insulating materials with a dielectric constant as low as possible in order to obtain device speed improvements through lower RC delay. We have investigated the electrical and structural properties of PTFE thin films obtained from Algoflon®-PTFE nanoemulsions, via spin coating deposition, followed by sintering . Films as thin as 160 nm with dielectric strength better than 4 MV/cm have been obtained.

Introduction

Replacing the current on-chip dielectric material such as silicon dioxide, which has a dielectric constant of approximately 4, with low dielectric constant materials can greatly improve the performance of high density ULSI device, not only by lowering line-to-line capacitance, but also by reducing cross-talk noise in the interconnect and alleviating power dissipation issues [1]. Several approaches have been considered including chemical processes to make porous the currently used silicon oxide [2] or the use of organic materials. Polytetrafluoroethylene (PTFE) has a very low dielectric constant and it is thermally stable above 400°C for short exposure time. Its outstanding heat resistance is related to high bond energy of C-C and C-F bonds, while low molecule polarity and low cohesive energy account for the excellent chemical resistance against a extremely broad range of aggressive chemicals. The combination of those properties together with high purity, very low dissipation factor, high hydrophobicity, makes it a very attractive candidate as interlayer dielectric material [3].

Usually, PTFE is manufactured by suspension or emulsion polymerisation [4]. Suspension reactor beads have a size of some millimetres that after post-treatment and milling can reduce to few microns, while emulsion particles have an average particle size of about 150 nm to 300 nm. With conventional polymerization technology,

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particles with a lower size, down to 100 nm, are obtained only with low conversion reactions [5]. In contrast with these conventional methods, latexes with particles from 10 to 100nm (fig. 1, as a representative example) are efficiently obtained with Ausimont technology of polymerization using perfluoropolyether microemulsions (PFPE μE) [6-8]. In comparison with other cases of PTFE microemulsion polymerisation [9] where low conversions and high surfactant concentration are used, with Ausimont technology PTFE latexes with small particle size are produced on an industrial scale, at high conversion, high latex concentration and with a relatively low surfactant content. Moreover, this polymerization technology allows to control not only the size of the PTFE primary particles, but also to change their morphology in order to get rod-like particles or spherical particles. In the case of rod-like particles, the length/diameter ratio (L/D) can be varied very easily in a large range (1–100), just changing the amount of classical "leverages" as surfactant concentration, comonomer content or molecular weight (MW) of the polymer. A detailed discussion on the nanoemulsion production process and on the related properties can be find elsewhere [10].

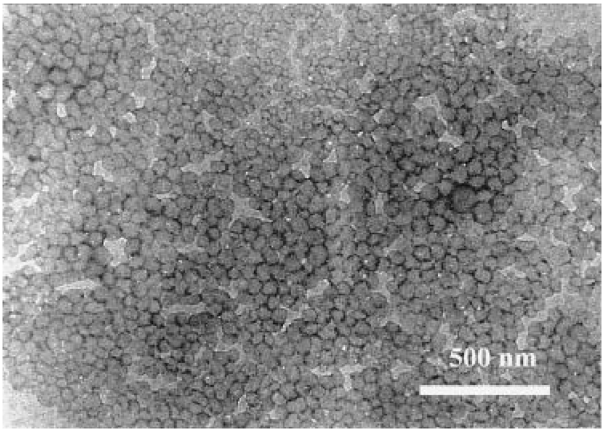

Figure 1. TEM picture of a modified medium molecular weight PTFE latex.

Experimental Part

Analytical Methods

Molecular weight has been evaluated using DSC and standard specific gravity according to the literature [11]. Melting point and the enthalpy of melting have been determined by Differential Scanning Calorimetry upon heating at 10 °C/min using a Perkin Elmer DSC 7. The degree of crystallinity has been calculated using 82 J/g for the heat of fusion of 100 % crystalline PTFE [12]. Melt viscosity of medium and low molecular weight samples has been measured using a Rheometric RMS 800 at 360 °C in the linear viscoelastic regime, while the melt viscosity of high molecular weight polymers has been measured at 360 °C using a home made shear creep apparatus [13] which allows the determination of steady state creep compliance and recovery. Particle radius has been measured through depolarized dynamic light scattering [14] with a BI 9000 correlator coupled with a BI 200 SM goniometer, both purchased from Brookhaven Instruments. The atomic force microscope (AFM) pictures have been taken with Thermomicroscopes Autoprobe CP in non contact mode using Ultralever tips with a nominal force constant of 2.8 N/m. Thickness has been determined by scratching the film with a razor blade and measuring the step height with the AFM. Current-voltage (I-V) characteristics are determined using 236 Keithley Source Measure Unit, while capacitance has been measured by 590 Keithley CV analyzer at 100 kHz and 1 MHz. I-V characteristic curves have been measured using pulsed voltage sweeps and continuous voltage sweep, from 0 to 110 V (corresponding to an applied field from 0 to 7 MV/cm on films as thick as 160nm). The two measurement techniques lead to equivalent results, but pulsed sweep is preferred in order to reduce heating effects.

Polymerization procedures

The PTFE nanoemulsions were produced through polymerization reactions carried out accordingly to the following general procedure. In a stainless steel water-steam jacketed reactor, de-ionized water and varying amount of perfluoropolyether microemulsion were added. The reactor was then evacuated and purged with tetrafluoroethylene. The agitation was started and the internal temperature increased to about 80°C, then the autoclave was pressurized with tetrafluoroethylene monomer (TFE). Finally, an aqueous solution of ammonium persulfate initiator was added to start the polymerization reaction and the pressure was kept constant by continuos feeding of TFE. After reaching the requested conversion, the reaction was stopped by interrupting the TFE feeding, the reactor de-pressurized and cooled, and a polymer dispersion was finally downloaded. The latexes produced by the above reaction procedure are stable colloidal dispersions of PTFE in water, optically clear at small particle size. The microemulsions used in this work have been prepared with perfluoropolyether oils and surfactant which are commercially available from Ausimont under the trade name Galden® and Fomblin®; microemulsion compositions have been already reported [8 , 10].

Materials

Three different classes of PTFE have been used in this work, exploring a broad range of of molecular weight and particle radius (R). High molecular weight polymer is an Ausimont commercial dispersion PTFE (Algoflon® D3015), while medium and low MW polymers have been specially prepared for this work using μE technology. As it is well known, the determination of PTFE molecular weight is difficult, being this polymer hardly soluble; however, following the literature [11], an estimate of the number average molecular weight of low (LMW), medium (MMW) and high MW (D3015) polymers leads to values about $5*10^4$, $5*10^5$ and $5*10^6$, respectively. The effect of the molecular weight is evident on both the degree of crystallinity and on the melt viscosity (table 1). It is well known that the mechanical resistance of sintered PTFE is strongly dependent on molecular weight [15], and particularly, low MW materials show a crystallinity degree higher than 90 %, which makes them brittle, while both medium and high molecular weight polymers are much less crystalline and tougher. The comparison of the melt viscosity of the three classes is also reported in fig. 2 where is evident the strong decrease of low shear viscosity induced by the decrease of the

Table 1

Molecular weight	**Sample ID**	**Tm (°C)**	**ΔH (J/g)**	**η_0 (Pa s)**	**R (nm)**
Low	LMW	327	79	$\approx 10^2$	18
Medium	MMW	326	39	$2 * 10^7$	34
High	D3015	327	39	$\approx 10^{10}$	104

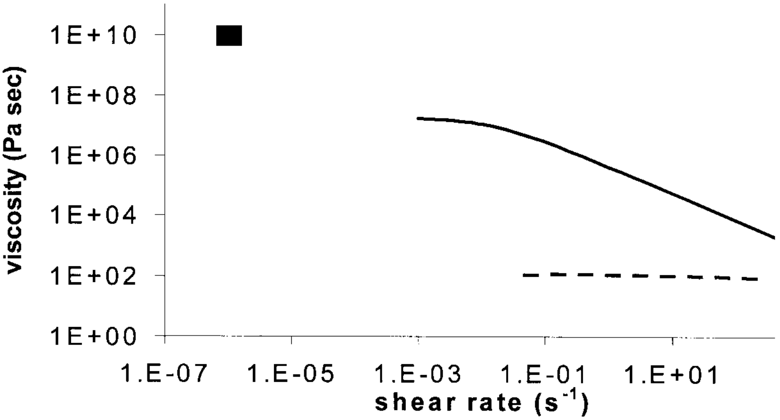

Figure 2. Melt viscosity at 360 °C. Algoflon D3015 (black square), MMW (continuos line), LMW (dashed line)

molecular weight. It is worth noting that MMW, as directly polymerized, has a melt viscosity in the range of the recently reported "melt processable PTFE " obtained by blending virgin and irradiated PTFE powders [16]. Therefore, the present set of materials shows how PTFE melt viscosity and crystallinity can be easily tuned directly in polymerization, allowing for a broad range of properties.

Preparation of PTFE Thin Films

The latexes were deposited by spin coating on n-doped silicon, in a class 1000 cleanroom. Non-ionic surface-active agents were added in order to promote the wetting on the hydrophobic surface of the silicon wafer. The substrate was then spinned at 6000 rpm for 2 min. A further spinning would not change film thickness or uniformity as confirmed by fringe interference observation. The film was then baked on a hot plate raising slowly the temperature from 20 ° C to 150 ° C in 30 min; this process is essential to avoid film cracking. The film was then heated over the PTFE fusion temperature in a rapid thermal annealing furnace to produce a uniform and continuous film. Sintering temperature was fixed at 400 °C and heating and cooling rate was set at 15 °C/sec.

The structural properties of the films were then studied by AFM and a strong dependence of morphology on the molecular weight was observed. In fig. 3 typical AFM images are reported for the three different molecular weights. In the top left panel

(a) we report a 80μm x 80μm topography image of a continuous film obtained with the LMW sample. Spherulitic domains are easily distinguishable; these spherulites are essentially bi-dimensional structures with a thickness of about 100 nm and a lateral size about 10 μm. The film at the nucleation centre is up to 50 % thicker than the rest of the spherulite, while the borders, despite being very evident, do not show a significant height change. In the top right panel (b) we report an AFM image for the same film on a smaller scale (10μm x 10μm), showing that at the spherulites borders the lamellae, are

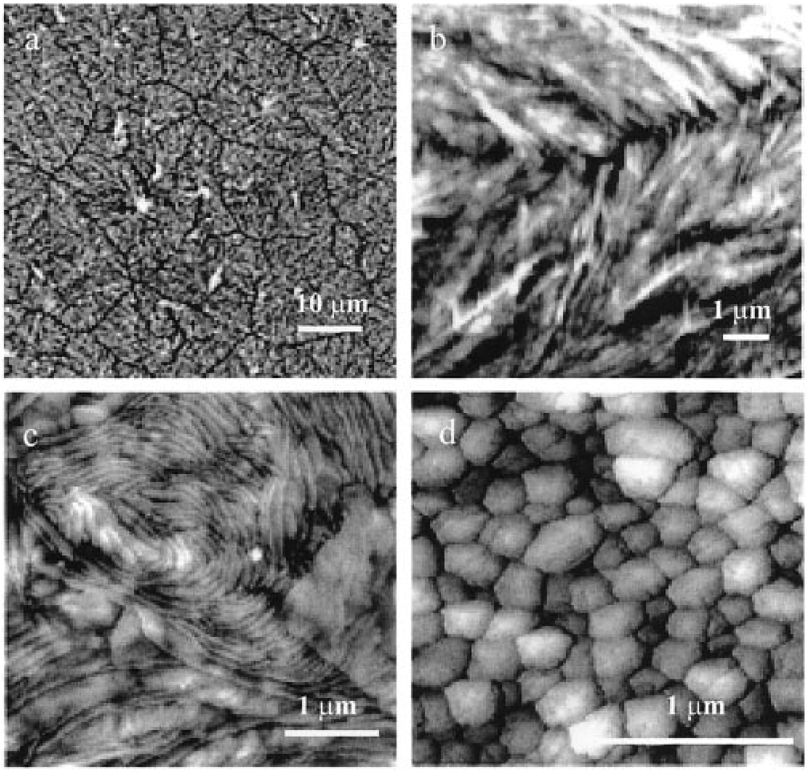

Figure 3. Typical AFM images (topography) for the three different MW polymers. a: a 80 μm x 80 μm image of low molecular weight PTFE. b: a 10 μm x 10 μm image of LMW film. c: a 5 μm x 5 μm image of MMW film. d: a 2 μm x 2 μm image of D3015. All images taken after the sintering cycle.

oriented in two different directions. The overall thickness inhomogeneity in the LMW film is, far from the nucleation center, of the order of ± 30nm with an average thickness of 90nm. In the bottom left panel (c) we report a 5μm x 5μm topography image of a continuous film obtained from PTFE nanoemulsion with medium molecular weight (MMW). In this case, lamellae oriented in different directions are present but no clear nucleation centre can be found. This film is smoother with a roughness of the order of ± 10nm on a film thickness of 120nm. In the bottom right panel (d) we show a 2μm x 2μm topography image of a film obtained from high molecular weight Algoflon® D3015. In this case, the sintering was not effective and the film is still composed of separate particles. For slower sintering process a partial fusion can be obtained but the films are still not continuous.

As a general conclusion, the most effective parameter in controlling the film morphology is the molecular weight, while only minor variations have been observed changing cooling cycles and inserting a slight amount of comonomer (data not shown).

Electrical properties

Metal-insulator-semiconductor capacitors (MIS-C), with PTFE as insulating film, were fabricated by standard lithographic techniques and electron beam evaporation. Aluminium circular electrodes were deposited with diameter ranging from 50 to 400 μm. The static dielectric constant ε_r was calculated from the capacitance with the

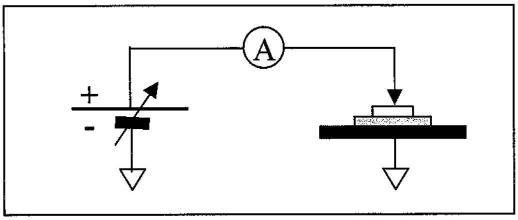

Figure 4. Experimental set up. The device under test is represented in section, with the three layers representing, from top to bottom, the aluminium contact, the PTFE film acting as insulator and the Silicon wafer

simple relation for flat armature capacitor:

$$C = \varepsilon_r \varepsilon_0 A/d$$

where *A* is the area of the MIS-C and *d* is the thickness of the PTFE layer, as determined with AFM. A schematic drawing of the MIS-C and of the measurement set up is reported in fig. 4. The values obtained for ε_r are 1.9 ± 0.2 in agreement with the bulk value (2.0); the uncertainty is mainly due to the inhomogeneity of film thickness. Before breakdown the leakage currents were always lower than the instrument sensitivity, that in the best condition was 10^{-12} A, corresponding to a current density of $1\text{x}10^{-9}$ A /cm^2 .

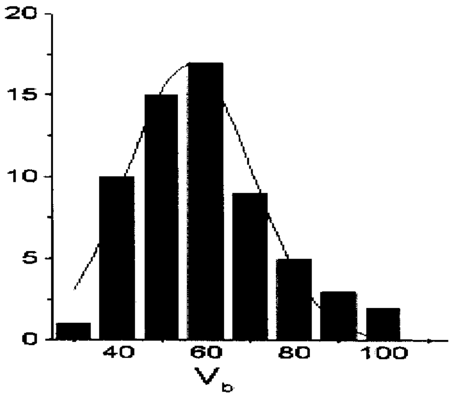

Figure 5. Typical distribution of breakdown events as a function of breakdown voltage. The shape of the distribution is well fitted by the Weibull distribution. Data refer to a MMW PTFE film.

Two different breakdown mechanisms were identified. Irreversible low field breakdown (E< 1MV/cm) without any visible damage on the film was observed only on LMW films and could be attributed to morphological defects and inhomogeneity due to the spherulites, and, therefore, to the low molecular weight of the PTFE. High field breakdown (E > 2 MV/cm) with thermal deformation due to current dissipation along the breakdown path occurred in both LMW and MMW films. The morphological and chemical effects of high field breakdown were locally studied by an analytical scanning electron microscope. The aspect of breakdown spots suggests that both the PTFE layer and the Aluminium layer reached temperatures above their melting point (327°C and 660°C, respectively) during the electrical discharge. No evidence of chemical reaction or compositional modification of the materials was observed after breakdown in the PTFE film.

The effect of purification from ionic species was also studied, together with the effect of siloxane addition into PTFE nanoemulsions during formulation. Ionic impurities arise from the polymerization process and can act as precursor or preferential path for the dielectric breakdown. Purification was obtained after treating a stabilized latex with a mixed ionic exchange resin and, then, filtering through a 5 μm cellulose filter. The siloxane addition into PTFE nanoemulsion has been reported to give better mechanical properties to film [17]; the maximum amount of tetraethoxysilane (TEOS) added (3% w/w) do not influence the value of ε_r.

Discussion

We analysed the breakdown data in the framework of the Weibull distribution that is generally accepted as the one which best fits dielectric strength data [18]. In the Weibull approach the layer under test is divided in n small elements, with unitary volume, which

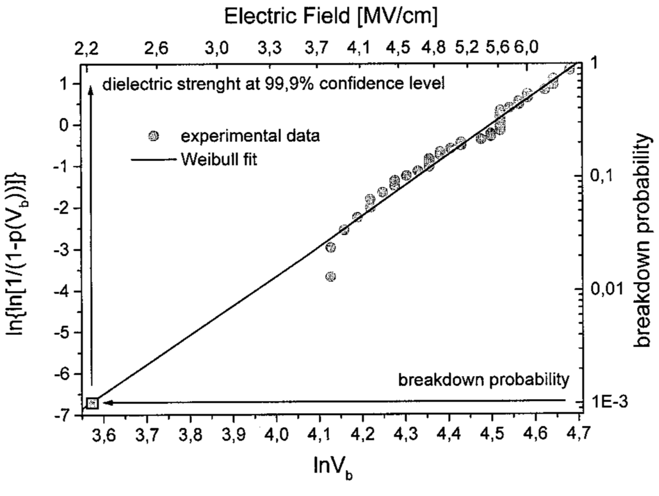

Figure 6. Weibull analysis of the breakdown data for MMW with 3% TEOS as a function of the given probability of failure.

have the same probability of not-breakdown, $e^{-(V/V_0)}$. The probability of not-breakdown of the whole layer is just the probability that none of the unitary element experience a breakdown. Therefore the breakdown probability for the whole layer is

$$P = 1 - e^{[-V/V_0]^m \cdot n}$$

where m is the Weibull modulus and accounts for the width of the distribution of breakdown events around its average value V_0 , and n represents the volume under test in arbitrary units. The conventional way to plot data makes uses of the following algebraic modification of the previous equation

$\ln(-\ln(1-P)) = m \ln V + \ln n - m \ln V_0$

Table 2. Dielectric properties of different MMW PTFE films.

sample	V_{bc}[a] [V]	h[a] [nm]	E_c[a] [10^6V/cm]	m[b]	sf_3[c]	E_3[c] [10^6V/cm]
MMW	64	160	4.0	4.5	5.1	0.8
MMW purified	90	190	4.7	8.5	2.3	2.0
MMW + TEOS	92	160	5.7	7.5	2.6	2.2

[a] V_{bc} is the mean or characteristic dielectric breakdown tension, h the film thickness, $E_c=V_{bc}/h$ is the mean dielectric strength.

[b] The Weibull modulus, m, obtained from the Weibull fit of the experimental data indicates a lower dispersion of data if higher.

[c] From the Weibull modulus derive the safety factor sf_3 that gives the allowable dielectric strength $E_3=E_c/sf_3$, corresponding to a failure probability of 10^{-3}.

The histogram in fig. 5 shows a typical Weibull distribution of the breakdown voltages for the MMW sample, and in fig. 6 the Weibull plot for the MMW sample added with TEOS 3% data as a function of the given probability of failure P is shown. The mean value of breakdown voltage (V_{bc}), and the slope of the fitting line (or Weibull modulus) m, can be experimentally determined.

In Table 2 we report the results of Weibull analysis for three MMW PTFE nanoemulsions as polymerized, purified and added with 3% TEOS. All films show average values of the dielectric breakdown voltage better than 4 MV/cm. Both the addition of TEOS and the purification induces an increase of both the average breakdown voltage and the Weibull modulus m. Therefore, both the treatments make the distribution of breakdown voltages peaked at higher values and narrower. As a consequence, the probability of breakdown at low voltage strongly decreases. In fact, values at a given confidence level can be extrapolated from the fit. From the Weibull modulus the safety factor sf_n for a given failure probability 10^{-n} can be calcuated. From sf_n, the corresponding allowable dielectric strength $E_n=E_c/sf_n$ is then obtained. The calculations for a failure probability of 10^{-3} are shown in table 2, where the increase of E_3 and the decrease of sf_3 with the treatments are evident. As a further example, the calculation of the allowable voltage corresponding to a failure probability equal to 10^{-7} (E_7) for the MMW purified nanoemulsion leads to E_7= 0.9 MV/cm, which correspond to 9 V for a film of 100 nm. This value is higher than presently used voltage in the application (3 to 5 V).

Conclusions

We produced homogeneous PTFE films as thin as 160 nm with dielectric strength better than 4 MV/cm, and studied the dependence of the structural and electrical film properties as a function of the synthesis parameters, polymer properties, dispersion formulation and application conditions. PTFE molecular weight is found to play a main role in terms of film uniformity and dielectric strength; this is due to its influence on the crystallinity of the film. The absence of ionic impurities and tetraethoxysilane (TEOS) addition improve the film behaviour. Preliminary chemical analysis of breakdown suggest an intrinsic mechanism, with short current discharge. In conclusion the obtained thin films could be considered as promising ultralow dielectric constant candidate for the future generations of IC devices.

Acknowledgements

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