Sensors and Actuators A, 41–42 (1994) 136–140

Applications of fluorocarbon polymers in micromechanics and micromachining

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Abstract

Several thin-film deposition and etching techniques of the polymer fluorocarbon are investigated and the resulting thin-film properties will be compared with those of commercially available bulk polytetrafluoroethylene The most promising deposition technique is performed in a conventional reactive ion etcher using a carbonhydrotrifluoride (CHF_3) plasma By changing the deposition parameters, control of the properties and step coverage of the deposited thin films within a certain range is possible, e g , uni-directional and conformal step coverage of deposited thin films can be obtained Etching is performed with the help of an evaporated aluminium oxide mask using an oxygen, nitrogen, or sulfurhexafluoride plasma for isotropic etching, or a CHF_3 plasma giving a directional etch profile The combination of the unique properties, deposition and etching techniques make fluorocarbon thin films a promising tool for micromachining, a number of applications will be discussed and demonstrated

Introduction

The linear fluorocarbon (FC) polymer polytetrafluoroethylene (PTFE) is better known under several trademarks such as Teflon®, Fluon®, or Hostaflon® Due to the many exceptional thermal, electrical, and chemical properties, it is an interesting material in all kinds of disciplines, such as microelectronics, micromechanics and (bio)chemistry Table 1 gives a summary of literature data [1–3] on the properties of PTFE These properties are considered indicative for a whole class of FC films

Applications in micromechanics generally require PTFE in the form of thin films and therefore we have investigated several deposition methods of PTFE-like films, i e , FC polymers with different chemical structures These films can be plasma-etched and their surface is modified during this etching This behaviour is important because many properties of the FC films are directly related to the surface and not to the bulk of the film The combination of the unique properties, deposition and etching techniques make FC films promising for micromechanical purposes A few applications will be demonstrated

Deposition techniques

Thin films of FC polymers can be made by several methods [1, 4–11] In this section spin-coating, plasma deposition, and e-beam evaporation will be discussed The adhesion of plasma-deposited films is much better than the spin-coated and evaporated films This is probably caused by the creation of dangling bonds at the surface of the underlying film when the film is deposited and the subsequent attachment of free radical copolymers ($CF_2^{\cdot\cdot}$) originating from the glow region

(i) *Spin-coating* FC thin films (down to 20 nm) can be spin-coated from a mixture of FC722® and FC40® [9] giving uniform and pinhole-free layers Figure 1 shows an example of an FC film lying on top of a silicon (Si) wafer This film is obtained by spinning an FC722 FC40 ≡ 1 1 mixture on the Si substrate for 60 s at 4000 rpm and baked for 5 min at 90 °C, resulting in a layer of 70 nm ± 1% The low surface free energy of the FC film reduces the adhesion to the substrate, adhesion is improved with the deposition of an intermediate layer, such as a polyimide film [4]

(ii) *Evaporation* FC films have also been deposited by e-beam evaporation of bulk PTFE Because of the directional nature of this technique, structures are only top-coated Figure 2 shows a SEM photograph of an aluminium structure covered with an evaporated FC film

(iii) *Plasma deposition* FC polymer films have been deposited via plasma polymerization of carbonhydrotrifluoride (CHF_3) in a commercially available reactive ion etcher (RIE) In the plasma mode (25 sccm CHF_3, 130 mTorr, 25 °C, 5×10^{-3} W/cm³, 0 V_{dc}) conformal coverage of three-dimensional structures is observed at a deposition rate of 5 nm/min Figure 3 shows an

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TABLE 1 Properties of bulk PTFE from literature data [1–3]

Electrical	
Volume resistivity	10^{16} Ohm m
Surface resistance	10^{16} Ohm
Bulk breakdown voltage	$\sim 4\times10^{7}$ V/m
Thin-film breakdown voltage	$\gg 4\times10^{7}$ V/m
Dielectric constant	2 1 (50 Hz–10 GHz)
Dissipation factor	0 0003 (50 Hz-10 GHz)
Chemical	
Stable and inert	(−190 up to +250 °C)
Oxidative stable	
Mechanical	
Young's modulus	4×10^{8} N/m^2
Bending strength	18×10^{6} N/m^2
Tensile strength	25×10^{6} N/m^2
Fracture strain	300–500%
Optical	
Refractive index	1 4
Optical transmission	>95%
Thermal	
Stable, unflammable and shape memory	
Minimum temperature	−190 °C
Maximum temperature	225 °C
Melting point	327 °C
Decomposition temperature	~400 °C
Melt viscosity	10^{10} Pa s
Thermal conduction	0 24 W/mK
Thermal capacity	1 05 J/gK
Expansion coefficient	8×10^{-5} 1/K
Physical	
Critical surface tension	18×10^{-3} N/m
Contact angle with water	108°
Friction coefficient with resp to steel	0 04
Specific gravity	2 20 g/cm^3
Non-permeable for fluids (except He)	

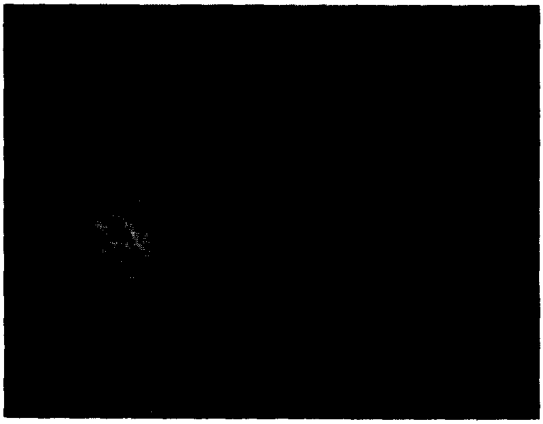

Fig 1 A spin-coated FC thin film on a silicon substrate

aluminium beam that is coated with an FC film with the same thickness on both sides of the beam

In the RIE mode (25 sccm CHF$_3$, 130 mTorr, 25 °C, 5×10^{-2} W/cm^2, target potential -100 V$_{dc}$) the film grows faster (26 nm/min) at the places which are directed to the plasma glow In Fig 4 an aluminium beam is completely surrounded by an FC film In this Figure three different phenomena are seen Firstly, the film is thicker at those places that are directed to the plasma glow This is probably caused by the formation of active sites due to impinging ions and/or photons from the plasma glow Secondly, the bad adhesion between the aluminium beam and its surrounding film is clearly seen Thirdly, at the edges of the beam a thicker layer has been deposited (arrow), this higher deposition rate might be caused by a higher flux of radicals that strikes the edges

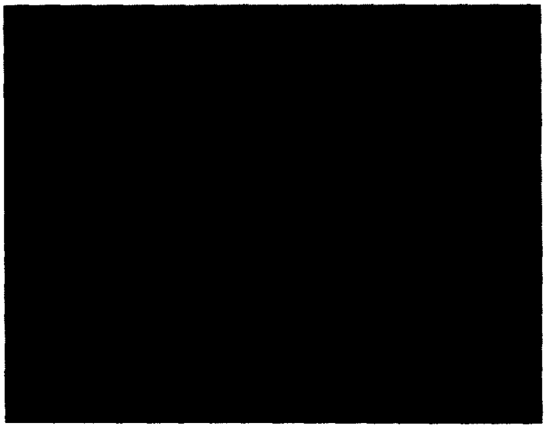

Fig 2 An evaporated FC thin film on top of an aluminium mask layer

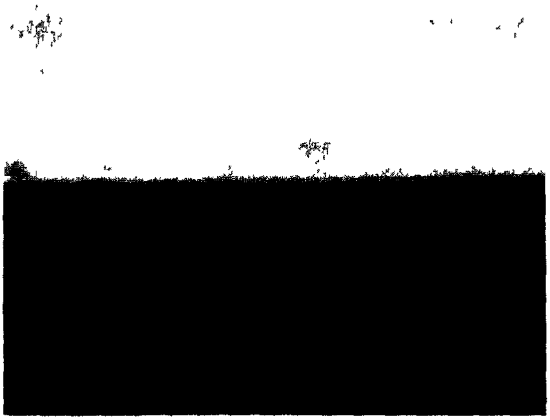

Fig 3 A plasma-deposited FC thin film (0 V$_{dc}$) giving a conformal step coverage over an aluminium beam

Unidirectional coverage of structures appears, just as was the case for the evaporated films, if an external bias (-400 V$_{dc}$) is applied in the RIE mode The deposition rate is higher than 50 nm/min in this mode In Fig 5 a free polysilicon beam is top-coated with an FC film

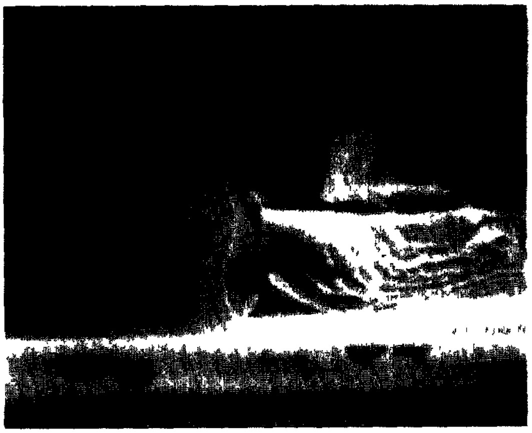

Fig 4 A plasma-deposited FC thin film (-100 V_{dc}) giving an enhanced deposition rate on the top of an aluminium beam The arrow indicates the thicker layer at the edges of the beam

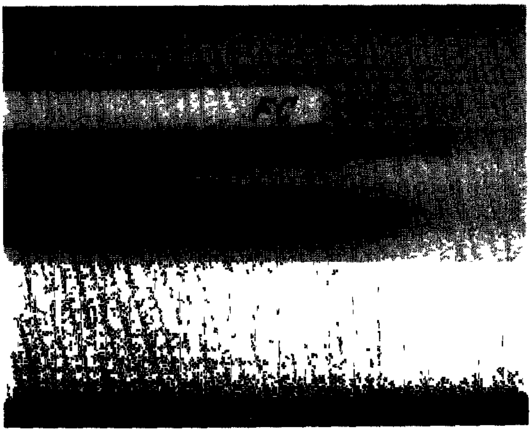

Fig 5 A plasma-deposited FC thin film (-400 V_{dc}) giving rise to a top-coated polysilicon beam

The FC films have been characterized by energy dispersive X-ray analysis (EDX), X-ray photoelectron spectroscopy (XPS), and Fourier-transform infrared spectroscopy (FT–IR) The analyses revealed that carbon is mainly bonded to two fluor atoms, although carbon bonded to one or three fluor atoms is also observed The contact angle, refractive index and the chemical properties were comparable with those of PTFE

Etching techniques

Fluorocarbon films can readily be etched isotropically in an RIE using an oxygen (O_2), nitrogen (N_2), or sulfurhexafluoride (SF_6) plasma and also in a carbonhydrotrifluoride (CHF_3) plasma in the lower pressure regime resulting in a unidirectional etch profile Thus, in the lower pressure regime the CHF_3 plasma etches an FC film whereas in the higher regime it will deposit a film FC films have an etch rate of ≈ 500 nm/min in O_2 plasmas and of ~ 100 nm/min in SF_6 plasmas, which is 60 times lower than that of silicon under the same conditions Inorganic materials, e.g, aluminium, are commonly used as a masking layer This versatility with respect to patterning leads to increased processing flexibility

Fig 6 A surface micromachined aluminium oxide beam An oxygen plasma is used to sacrifice the underlying FC thin film

(i) *Spin-coated films* Direct patterning of FC film with photoresist is not possible because, due to the low surface free energy and high wetting angle of the FC film, the spin-coated resist cannot adhere at the FC surface However, evaporated aluminium oxide (Alox) does adhere and can be patterned In Fig 6 an FC film is coated first with an aluminium oxide film and after patterning the aluminium oxide mask, the FC film is isotropically etched with an O_2 plasma The isotropic underetch is clearly observed

(ii) *Evaporated and plasma-deposited FC films* E-beam evaporated and plasma-deposited FC films can be patterned directly with photoresist This difference with respect to the spin-coated films might be caused by the rougher surface of the plasma-deposited films

Applications

A number of possible applications of FC films will be discussed and demonstrated below

(i) *Passivation layer* Micromechanical structures and electronic circuitry can be coated with FC polymer to prevent corrosion In this way, high-quality mirrors, microgrippers, and electrostatic actuators can be fabricated Because of their chemical inertness and low surface free energy, FC films are biocompatible and could be used as a passivation layer in the medical and chemical analysis systems For example, an ion-sensitive field-effect transistor (ISFET) [12] was coated with a spin-coated and a plasma-deposited film in order to decrease the pH sensitivity It was found [13] that the pH sensitivity of such a so-called reference FET (REFET) was decreased by a factor six, which makes it a possible standard REFET Moreover, no CO_2 response of this REFET was measurable indicating that the film is non-porous and pinhole free

(ii) *Insulator layer* FC films have a high resistivity, therefore only very thin layers are required for electrical insulation Moreover, because of their high resistivity and hydrophobic nature, FC films are suitable as electrets in, e g , micromachined silicon microphones [14] It was found [13] that the spin-coated FC electret is as good as the silicon dioxide/hexamethyldisilizane (SiO_2/HMDS) electret [15] When charging the FC electret beyond the breakdown voltage (4×10^7 V/m), the electret voltage dropped quickly to this voltage where it stabilized It was also found that SiO_2 electrets treated with an FC passivation layer do not discharge when wetted, while those with HMDS do

(iii) *Sacrificial layer* Because very thin layers (<20 nm) can be deposited with conformal step coverage and because selective etchants are known, the FC polymers are excellent sacrificial layers to be used in surface micromachining This is demonstrated in Fig 6 where a 70 nm thick, spin-coated FC film beneath an evaporated aluminium oxide beam is isotropically etched under with the help of a dry O_2 plasma etch The etch rate is approximately 0.5 μm/min

(iv) *Structural layer* FC films are practically unbreakable and chemically inert For this reason they are useful as mechanical construction material in micromechanics, e g , beams or membranes The low Young's modulus is required for devices generating large deformation under moderate forces Because the films do not stick to almost any substrate, special construction methods must be developed (e g, mechanical anchoring) In Fig 7 an FC beam is shown that is made of a plasma-deposited FC film which is patterned with the help of an O_2 plasma and an aluminium oxide mask

(v) *Anti-sticking layer* FC surfaces have extremely low free energy and, as a result, they tend to have non adhesive character and low coefficients of friction Therefore, FC films can be used as a coating over a solid surface to prevent or reduce adhesion when a material is brought into contact with the solid, e g , self-lubricating bearings, pumps, pipelines and valves in the chemical industry In Fig. 8 an isotropically etched silicon flow channel is coated with a very thin plasma-deposited FC layer Other opportunities are the release of micromechanical structures without the use of a sacrificial layer Figure 9 shows the bending of an aluminium beam which is situated directly on top of a spin-coated FC film This structure can be used as the electrostatically driven element in the active joint [16] It is fabricated by applying an FC film on a silicon substrate and an aluminium layer on top of this Now, when the aluminium is patterned the beams will bend directly because of their, built-in, intrinsic stress without etching the FC layer

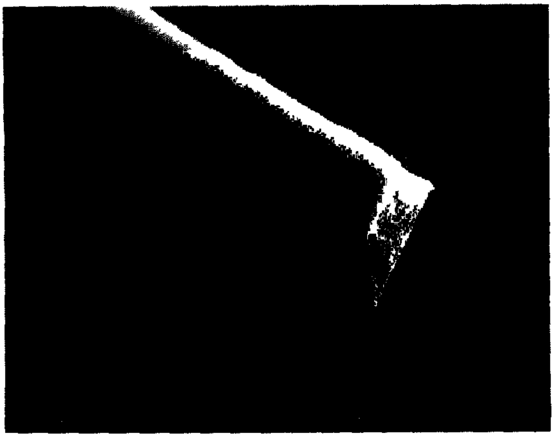

Fig 7 An FC beam, lying on top of a silicon substrate, constructed with the help of an aluminium oxide mask layer and an oxygen plasma

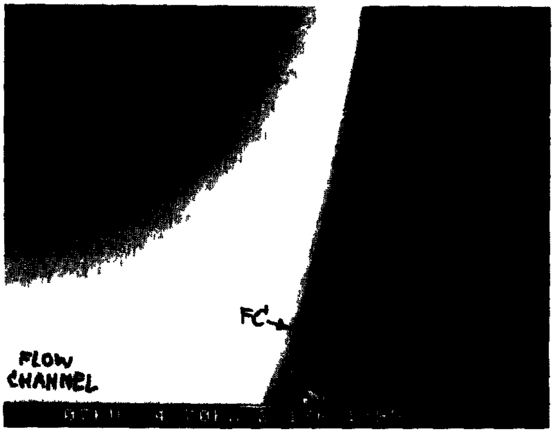

Fig 8 A silicon flow channel coated with a plasma-deposited FC thin film

Although the opportunities of the following examples are not demonstrated yet, they are also of interest in micromechanics and microelectronics

(i) FC films are transparent and are found to make excellent optical films for, e g , fibres and planar waveguides Teflon AF2400® [10] can be used as a low refractive-index (1 29¹) coating for optical devices

(ii) Fluorinated polymers are available for imparting oil and water resistance to micromechanical structures because of their nonwettability We can imagine a

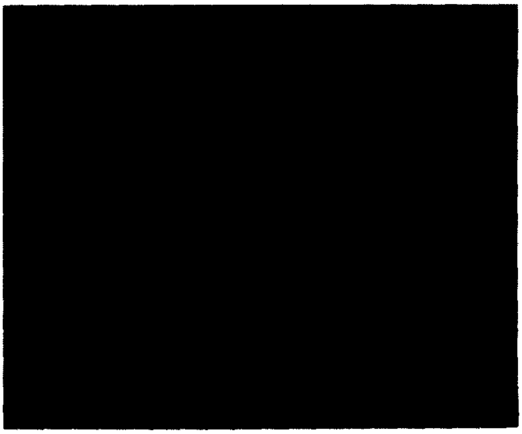

Fig 9 The bending of aluminium beams released directly from the substrate, without the use of a sacrificial layer, due to the underlying FC thin film

number of unique uses for materials of this type, e g, adhesives with selective bonding properties and barrier materials to prevent the spreading of liquids from points of contact on ball bearings, motors, and other devices

(iii) The low Young's modulus makes it possible to use FC films as a 'rubbery' coating for microvalves in preventing leakage of fluids

(iv) FC films can be compounded with other plastics or metals by simultaneously sputtering metals in the reactor chamber during PECVD deposition of FC films [11]

Conclusions

The usefulness of FC polymers in micromechanics has been demonstrated Three different kinds of deposition techniques are treated spin coating, evaporation, and plasma deposition Especially the plasma-deposited films are very attractive because it is possible to cover structures in different ways Etching is performed in the same plasma reactor that is used for deposition and it is possible to etch thin FC films unidirectional as well as isotropic Many materials, mostly inorganic, are known to act as a masking layer in order to copy the geometry of the developed photoresist into the FC films The unique properties and the diversity in deposition, etching, and masking materials make the use of FC films in micromechanics and microelectronics very simple and straightforward

Acknowledgements

The authors are grateful to Geert Langereis, Wouter Olthuis, and Piet Bergveld for putting their measurement results on the REFET and electret to their disposal Special thanks to Bert Otter for making the SEM photos and Erwin Berenschot for his work on the active joint These investigations in the programme of the Foundation for Fundamental Research on Matter (FOM) have been supported by the Netherlands Technology Foundation (STW)

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