ELSEVIER

Thin Solid Films 395 (2001) 288–291

thin solid films

www.elsevier.com/locate/tsf

Hot-wire chemical vapor deposition (HWCVD) of fluorocarbon and organosilicon thin films

K.K.S. Lau, H.G. Pryce Lewis, S.J. Limb, M.C. Kwan, K.K. Gleason*

Department of Chemical Engineering, Massachusetts Insitute of Technology, Cambridge, MA, USA

Abstract

HWCVD affords the capability to synthesize fluorocarbon and organosilicon thin films. These two classes of materials are of interest for a wide range of applications, including low dielectric constant coatings for microelectronic interconnection, 'dry' photoresists, directly patternable dielectrics for lithographic production of integrated circuits, insulating biomaterials for implantable devices with complex topologies and small dimensions, low friction coatings, and semipermeable membranes. HWCVD from hexafluoropropylene oxide (C_3F_6O) dramatically reduces cross-link and defect concentrations in fluorocarbon coatings, producing films which are spectroscopically indistinguishable from bulk polytetrafluoroethylene (PTFE, Teflon™). Organosilicon films can be deposited from cyclic precursors such as octamethylcyclotetrasiloxane (D_4) at extremely high rates (>2 μm/min) by HWCVD. The bonding structure of HWCVD organosilicon films is substantially different from both their plasma enhanced CVD (PECVD) counterparts and bulk siloxane polymers, such as poly(dimethysiloxane) (PDMS).

Keywords: Hot-wire deposition; Fluorocarbon; Organosilicon

1. Introduction

Both fluorocarbon and organosilicon films find extremely diverse applications because of their unique electrical, chemical and surface properties. Fluorocarbon films are currently being evaluated as dielectric interconnects in microelectronic circuits and as passivation coatings in clinical devices [1,2]. Potential applications of organosilicon CVD thin films include biocompatible coatings for medical implants [3], semipermeable membranes [4], integrated optical devices [5], dielectric films [6], and abrasion and corrosion resistant coatings [7].

HWCVD represents an alternative to PECVD for depositing both fluorocarbon [8] and organosilicon [9] thin films. Plasma exposure is entirely eliminated by HWCVD, a process in which a fluorocarbon or organosilicon gas is thermally decomposed over a hot surface while the substrate remains cool. In HWCVD, substrate temperature and gas precursor breakdown temperature are independently controlled. This is a distinct difference from conventional thermal CVD which involves heating the susceptor on which the substrate is placed.

HWCVD overcomes some of the processing constraints of having a directly heated substrate. The advantage of being able to achieve high temperature gas decomposition, yet film deposition on a substrate at room temperature, is threefold. First, absorption limited deposition processes can be employed, since lower substrate temperatures enhance such mechanisms. Second, temperature sensitive substrates can be coated without difficulty, and film stresses due to temperature mismatch during and after deposition can be eliminated. Finally, significantly higher filament temperatures can be attained with low power consumption, permitting a more extensive range of CVD chemistries to be explored.

In this paper, HWCVD of fluorocarbon and organosilicon thin films in our laboratory [10–16] is reviewed.

* Corresponding author. Department of Chemical Engineering, Massachusetts Institute of Technology, Room 66-352, Cambridge, MA 02139, USA. Tel.: +1-617-253-5066; fax: +1-617-253-7983.
E-mail address: kkgleasn@mit.edu (K.K. Gleason).

0040-6090/01/$ - see front matter
PII: S0040-6090(01)01287-1

Fig. 1. Schematic of the HWCVD chamber. Showing gas inlet through upper showerhead, pyrolysis on square filament array, and deposition onto a wafer substrate resting on the bottom electrode. The gas pump out is toward the back side of the chamber.

2. Experimental

For the fluorocarbon films, undiluted hexafluoropropylene oxide [HFPO; $CF_3CF(O)CF_2$] was used as the precursor gas. Organosilicon thin films were grown from octamethylcyclotetrasiloxane, $[(CH_3)_2SiO]_4$, also known as D_4 from the commonly used nomenclature of D for $–(CH_3)_2SiO–$. D_4 is a monomer which is commonly used in the base catalyzed, liquid phase ring-opening polymerization to PDMS.

Table 1
Typical process conditions for HWCVD

CVD parameter	Fluorocarbon	Organosilicon
Filament temperature (°C)	400–500	800–1000
Filament material	NiCr (80/20)	Ta
Substrate temperature (°C)	25	25
Pressure (torr)	0.4–1.2	0.2–1.0
Flow rate (sccm)	10–400	1–15
Feed gas	HFPO	D_4

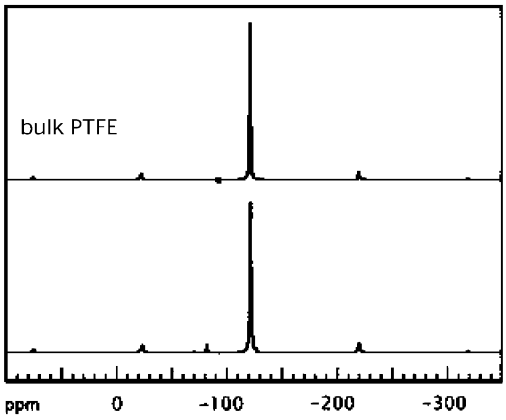

Fig. 2. Solid-state ^{19}F-NMR of HWCVD fluorocarbon film (bottom) and PTFE (top).

Films were deposited onto silicon wafers by HWCVD in a custom built vacuum chamber (Fig. 1) having backside water cooling on the substrate. The filament-to-substrate distance was maintained at 2.5 cm for the fluorocarbon films, and 1.0–1.5 cm for the organosilicon films. Table 1 summarizes the other HWCVD process parameters.

X-Ray photoemission (XPS) survey and C1s scans were obtained at a takeoff angle of 45° using a Mg $K\alpha_{1,2}$ source on a Perkin-Elmer 5100 instrument. Two spectra were run, a high resolution C1s and a low resolution (e survey) over a broader energy range. A Nicolet 860 was used to obtain the Fourier transform infrared (FTIR) spectra. High-resolution solid-state nuclear magnetic resonance (NMR) experiments were performed with a Chemagnetics 3.2-mm magic angle spinning probe at a field of 6.3 T.

3. Results and discussion

Figs. 2 and 3 compare the ^{19}F-NMR and FTIR spectra, respectively, for a film grown by HWCVD of HFPO to

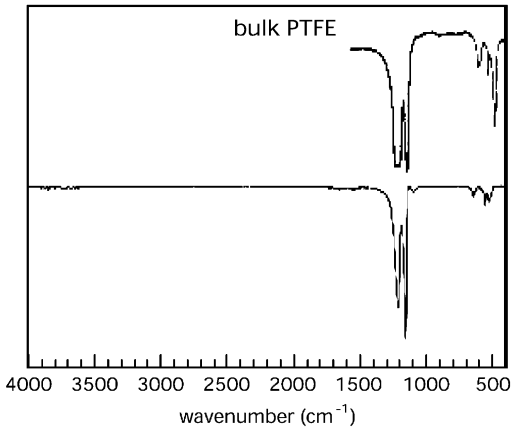

Fig. 3. FTIR of HWCVD fluorocarbon film (bottom) and PTFE (top).

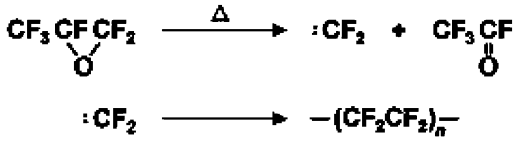

Fig. 4. Reactions for the pyrolysis of HFPO and polymerization of difluorocarbene.

bulk PTFE, showing the similarity in chemical structure of the two types of materials.

The precursor gas HFPO has a well-known thermal decomposition pathway (Fig. 4) which commences at a fairly low temperature of 150°C [17]. The product, difluorocarbene, can then polymerize to form linear CF_2 chains [18].

Thus, HWCVD fluorocarbon films differ from their counterparts grown by plasma enhanced chemical vapor deposition (PECVD). The PECVD films generally have a F/C ratio of ~1.5 as compared to 2 for PTFE [–$(CF_2)_n$–]. In addition, the PECVD films contain dangling bonds (free radicals), double bonds and cross-links. These defects degrade the film electrical and mechanical properties, and also contribute to the aging of these materials [19]. Exposure of the growth surface to the plasma plays a key role in defect formation. Plasma exposure is entirely eliminated by HWCVD.

Using HWCVD from D_4, high deposition rates (up to 2.5 μm/min) for organosilicon thin films could be achieved [11]. Fourier transform infrared spectroscopy (Fig. 5) verified that the deposited films had the same functional groups as a PDMS standard, though with a measurably lower methyl concentration. Marked differences in the IR intensity can be seen at 2964 cm^{-1} (asymmetric C–H methyl stretch), 2906 cm^{-1} (symmetric C–H methyl stretch), and at 1410 cm^{-1} (C–H methyl bending modes). No C–C cross-linking is detected, since such a rearrangement would result in the appearance of new peaks in the C–H stretch region at lower wave numbers corresponding to sp^3-CH_2. Such sp^3-CH_2 peaks are often observed in PECVD films. Thus, the HWCVD materials differ from both PDMS and PECVD films.

XPS showed that a typical film had an elemental composition of C:Si:O/1.5:1:1, confirming the loss of methyl groups. ^{29}Si-NMR suggested the existence of Si–Si cross-linking in the film, also consistent with the loss of methyl groups [20].

The ability of HWCVD to extend the compositional range beyond that of PECVD films can ultimately improve the resulting properties. The molecular architectures uniquely achieved by HWCVD enable all-dry, resistless patterning of fluorocarbon low dielectric constant films, using supercritical CO_2 as the development medium [21]. Lines and spaces defined by electron beam lithography at 0.25-μm resolution are shown in Fig. 6.

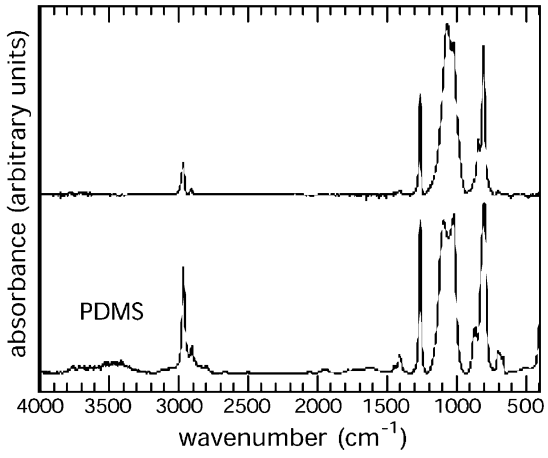

Fig. 5. FTIR of HWCVD organosilicon film (top) and PDMS (bottom).

In addition, the absence of plasma driven densification processes can lead to the incorporation of porosity in the HWCVD films, further reducing their effective dielectric constant [16]. Under HFCVD conditions which limit nucleation, a unique morphology can arise in HWCVD fluorocarbon films, as shown in Fig. 7. This morphology clearly is the source of the porosity, which further lowers the dielectric constant of these films.

4. Conclusions

Fluorocarbon films have been deposited by HWCVD and possess a chemical structure similar to poly(tetrafluoroethylene). Organosilicon films can be deposited from cyclic precursors such as octamethylcyclotetrasiloxane (D_4) at extremely high rates (>2 μm/min) by HWCVD. The bonding structure of HWCVD organosilicon films is substantially different from both their PECVD counterparts and bulk siloxane polymers, such as poly(dimethylsiloxane).

In contrast to plasma enhanced CVD, the HWCVD process does not involve any ion bombardment or UV irradiation, thus eliminating the possibility of related atomic rearrangements and defects. The ability to grow

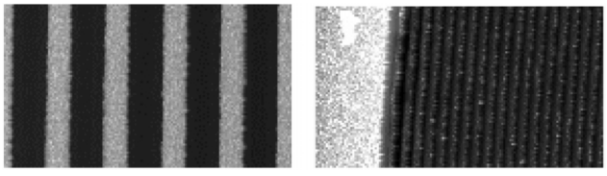

Fig. 6. HWCVD fluorocarbon low dielectric constant film directly patterned at 1.0 (left) and 0.25 (right) μm resolution.

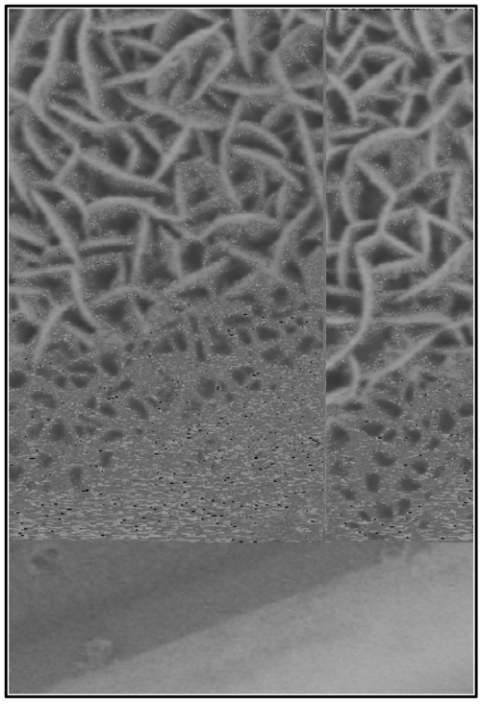

Fig. 7. Scanning electron micrograph of the HWCVD porous fluorocarbon film at the edge of the silicon wafer substrate (bottom right). The tilt angle makes it possible to observe both the surface morphology (top left) and porosity through the thickness of the layer.

fluorocarbon and silicone thin films by HWCVD reveals that ion bombardment, which is often cited in discussions of PECVD mechanisms as being essential to the creation of active sites for film growth [22], is in fact not necessary for the deposition of these materials.

Acknowledgements

We gratefully acknowledge the NIH (Contract N01-NS-3-2301), NSF (CTS-9057119) and the NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing for funding this work. This work made use of MRSEC Shared Facilities supported by the NSF (DMR-9400334).

References

[1] K. Endo, T. Tatsumi, Y. Matsubara, T. Horiuchi, Jpn. J. Appl. Phys. Pt. 1 37 (1999) 1808.
[2] B.D. Ratner, A. Chikoti, G.P. Lopex, Plasma deposition and treatment for biomedical applications, in: R. d'Agostino (Ed.), Plasma Deposition, Treatment, and Etching of Polymers, Academic Press, San Diego, 1990.
[3] A.S. Chawla, Biomaterials 2 (1981) 83.
[4] J. Sakata, M. Yamamoto, M. Hirai, J. Appl. Polym. Sci. 31 (1986) 1999.
[5] P.K. Tien, Rev. Mod. Phys. 49 (1977) 361.
[6] M.R. Wertheimer, T.S. Ramu, U.S. Patent no. 4,599,578, 1986.
[7] T. Wydeven, Appl. Opt. 16 (1977) 717.
[8] K.K. Gleason, S.J. Limb, H.H. Sawin, E.F. Gleason, D.J. Edell, Chemical Vapor Deposition of Fluorocarbon Polymer Thin Films, U.S. Patent no. 5,888.591, 1999.
[9] K.K. Gleason, M.K. Kwan, Pyrolytic Chemical Vapor Deposition of Silicone Films, U.S. Patent no. 6,045,877, 2000.
[10] S.J. Limb, C.B. Labelle, K.K. Gleason, D.J. Edell, E.F. Gleason, Appl. Phys. Lett. 68 (1996) 2810.
[11] M.C. Kwan, K.K. Gleason, Chem. Vapor Deposition 6 (1997) 299.
[12] S.J. Limb, K.K.S. Lau, D.J. Edell, E.F. Gleason, K.K. Gleason, Plasmas Polym. 4 (1999) 21.
[13] K.K.S. Lau, K.K. Gleason, J. Fluorine Chem. 104 (2000) 119.
[14] K.K.S. Lau, C.B. Labelle, K.K. Gleason, J. Dielectrics 1 (1999) 51.
[15] K.K.S. Lau, J.A. Caulfield, K.K. Gleason, Chem. Mater. 12 (2000) 3032.
[16] K.K.S. Lau, J.A. Caulfield, K.K. Gleason, J. Vac. Sci. Technol. A 18 (2000) 2404.
[17] H. Millauer, W. Schwertfeger, G. Siegemund, Angew. Chem. Int. Ed. Engl. 24 (1985) 161.
[18] K.K.S. Lau, K.K. Gleason, B.L. Trout, J. Chem. Phys. 113 (2000) 4103.
[19] H. Yasuda, J. Macromol. Sci. Chem. A 10 (1976) 383.
[20] H.G. Pryce Lewis, T.B. Casserly, K.K. Gleason, J. Electrochem. Soc. (submitted).
[21] G.L. Weibel, H.G. Pryce Lewis, K.K. Gleason, C.K. Ober, Polym. Preprints 41 (2000) 1838.
[22] A. Wrobel, M. Wertheimer, in: R. d'Agostino (Ed.), Plasma Deposition, Treatment, and Etching of Polymers, Academic Press, San Diego, 1990.