

Deposition of Ultrathin Fluoropolymer Films on Si(100) and GaAs(100) Surfaces by RF Magnetron Sputtering of Poly(tetrafluoroethylene-co-hexafluoropropylene)

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Dielectric fluoropolymer films of 10–50 nm in thickness were deposited on the (100)-oriented single-crystal silicon and gallium arsenide wafers via RF plasma sputtering of a poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) target. X-ray photoelectron spectroscopy, time-of-flight secondary ion mass spectrometry, water contact angle measurement, and Fourier transform infrared spectroscopy results indicated that the chemical composition and molecular structure of the sputter-deposited polymer films depended strongly on the type of the sputtering gas used. The dielectric constant of the argon-plasma sputter-deposited fluoropolymer film is about 2.1, which is comparable to those of the pristine FEP and poly(tetrafluoroethylene) films. It was shown that the argon plasma sputter-deposited FEP (s-FEP(Ar)) film as thin as 6 nm could effectively passivate the HCl-etched GaAs(100) substrate under atmospheric conditions. The growth of the surface oxide layer was effectively hindered by the ultrathin s-FEP(Ar) barrier when the passivated GaAs(100) surface was exposed to the ambient air for a prolonged period of time. Peel adhesion test results suggested that all of the sputter-deposited films adhered strongly to the Si(100) and GaAs(100) surfaces.

Introduction

With the continuous decrease in the dimension of integrated circuits, the signal delay caused by the interconnects has become more important than that induced by the intrinsic gate-to-gate delay.^{1,2} One method of lowering the interconnect delay is through the use of highly conductive metals and low capacitance dielectrics. Fluoropolymers are promising materials for interlayer dielectrics because of their low dielectric constants (low κ 's), low dissipation factors, and high thermal stability.³ The hydrophobic nature of the fluoropolymer films also makes them good candidates for barriers and passivation layers. Unfortunately, most of the fluoropolymers suffer from limited processability.⁴ To overcome the processability problem, a number of fine studies have been carried out to prepare and deposit fluoropolymer films using the gas-phase processing techniques, in particular, the plasma enhanced chemical vapor deposition (PECVD) and plasma polymerization techniques.^{5–8} In the plasma polymerization techniques, the polymer film is deposited from the monomer. A variety of fluoro monomers, either in the liquid or gas state, have been employed to deposit the corresponding fluoropolymers.

An alternative approach to PECVD and plasma polymerization for preparing fluoropolymer films involves the sputtering of a solid fluoropolymer target by a gas plasma. Recombination of the sputter-generated species and segments on a substrate under high vacuum gives rise to the desired fluoropolymer deposit. The process is, thus, similar to that commonly used for the sputtering deposition of metal film in the microelectronics industries. Fine works on the deposition of fluorocarbon films via radio frequency (RF) plasma sputtering of a poly(tetrafluoroethylene) (PTFE) target have appeared since the 1970's.^{9–13} The effects of various experimental parameters, such as sputtering gas, voltage, RF input power, magnetic field, target/

substrate distance, pressure, and gas composition, on the properties of the deposited fluorocarbons have been investigated.^{11,13–19} With physicochemical and dielectric properties comparable to those of PTFE, poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) is another potential dielectric polymer for high-frequency applications, provided that the processability issue of FEP can also be resolved. In this regard, RF sputtering deposition of FEP films appears to be an attractive approach and warrants a detailed study as in the case of RF sputtering deposition of PTFE.

On the other hand, GaAs is one of the most important compound semiconductors. In comparison with the Si-based devices, the compound semiconductors have the advantage in radiation resistance and low power dissipation.²⁰ However, the very high density of surface and interface states has limited the wide spread application of GaAs as a compound semiconductor. To improve the performance of the GaAs substrate, S-containing agents have been widely used to reduce the surface recombination velocity and the pinning of the surface Fermi level.^{21–23} However, the sulfides-passivated GaAs surface is chemically unstable under ambient conditions. The unpinned GaAs surface oxidizes gradually in the presence of light and oxygen.^{24,25} Furthermore, the formed As₂S₃ is somewhat soluble in water.^{26,27} Nevertheless, coating of GaAs with stable octadecylthiol monolayers in aqueous electrolytes has been reported.²⁸ Passivation of the GaAs surface by nitridation with N₂–H₂ remote plasma has also been carried out.²⁹

In addition to very low dielectric constants, the highly cross-linked and hydrophobic nature of the sputter-deposited fluoropolymer films also make them good barriers and passivation layers for semiconductors and microelectronic components. Accordingly, deposition of dielectric fluoropolymer films on Si(100) surfaces by RF magnetron sputtering of an FEP target is first carried out. The chemical composition and structure, as well as the adhesion and dielectric properties, of the sputter-deposited fluoropolymer films to serve as the interlayer dielec-

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tics on silicon are characterized. Particular attention is paid to the effect of sputtering gas on the physicochemical and dielectric properties of the deposited fluoropolymer films. Finally, the ability of the sputter-deposited and ultrathin FEP film to serve as a barrier in passivating the unstable GaAs(100) surface is investigated.

Experimental Section

Materials. Single-crystal Si(100) wafers, having a thickness of about 650 μm and a diameter of 150 mm, were obtained from Unisil Co. of Santa Clara, CA. The as-received wafers were polished on one side and doped as p-type. The Si wafers were sliced into chips of about 5 mm \times 5 mm in dimension. To remove the organic residues from the surface, the silicon substrates were washed with the "piranha" solution, a mixture of 98 wt % concentrated sulfuric acid (70 vol %) and hydrogen peroxide (30 vol %). After rinsing with copious amounts of doubly distilled water, the Si substrates were dried in a N_2 stream. The GaAs(100) wafers, having a thickness of about 300 μm and a diameter of about 50 mm, were obtained from Wafer World Inc., Ft. Lauderdale, FL. The as-received wafers were polished on one side and doped with Si. The wafers were also sliced into chips of about 5 mm \times 5 mm. The GaAs substrate was sonicated in ethanol for 10 min and then dried in an argon stream. The GaAs substrate was subsequently dipped into concentrated HCl (37 vol %) for 2 min to remove the surface oxide layer.²⁸ The FEP sputtering target of 150 mm in diameter and 0.05 mm in thickness was cut from an FEP film. The latter was obtained from Goodfellow Ltd., of Cambridge, U.K. The FEP target was backside-bonded to a copper plate before being installed into the sputtering system.

Radio Frequency (RF) Sputtering of FEP onto Si(100) and GaAs(100) Substrates. The RF plasma sputtering process was carried out on a triple-cathode S-2000 sputtering system, assembled by Korea Vacuum Technology of Seoul, Korea. The FEP target was installed in the RF magnetron sputtering gun powered by a Comdel CX-600S RF generator (RF = 13.56 MHz). The sputtering process was preprogrammed and microprocessor-controlled. After the substrates were fixed on the rotary sample stage, the base pressure of the sputtering chamber was pumped down to below 3×10^{-5} Torr by a turbo molecular pump, backed by a high capacity mechanical pump. The sputtering gas (purified Ar, CF_4 , N_2 , H_2 , or O_2) was then introduced into the sputtering chamber at a flow rate of 30 standard cubic centimeter per min (sccm). The flow rate of the sputtering gas was controlled by an MKS mass flow controller (MFC). The distance between the substrate and the target was about 13 cm. The silicon or GaAs surface was precleaned and preactivated by a 50-W pure gas plasma for 1 min. During the precleaning process, the FEP target was covered by a stainless steel shutter. The FEP target surface also underwent a sputter-cleaning process for 30 s, with the substrate surface covered by a shutter. The system pressure was maintained at 12×10^{-3} Torr during preactivation of the substrate and precleaning of the target, as well as during the sputter deposition process, by the MKS 600 automatic pressure controller. The sputter deposition process was carried out at an RF power of 150 W for 10 min on Si(100) surface and 80 s on the GaAs(100) surface. The ionic fragments had energies varying from 5 to 30 eV.¹⁶ After sputtering deposition, the substrate was kept under vacuum for 1–2 h to allow the aging of the residual free radicals in the film.³⁰ The complete annihilation of the radicals was indicated by the lack of any reaction with oxygen after the film was exposed to the atmosphere.

Surface Characterization. The chemical compositions of the pristine FEP film and the sputter-deposited polymer films on the preactivated Si(100) and GaAs(100) surfaces were determined by X-ray photoelectron spectroscopy (XPS). The XPS measurements were carried out on the AXIS HSI spectrometer (Kratos Analytical Ltd., Manchester, England) with a monochromatized Al $\text{K}\alpha$ X-ray source (1486.6 eV photons) at a constant dwell time of 100 ms and a pass energy of 40 eV. The anode voltage and current were set at 15 kV and 10 mA, respectively. The pressure in the analysis chamber was maintained at 5×10^{-8} Torr or lower during each measurement. The samples were mounted on the sample stubs by means of double-sided adhesive tapes. The core-level signals were obtained at a photoelectron takeoff angle (with respect to the sample surface) of 90°. All binding energies (BEs) were referenced to the C 1s hydrocarbon peak at 284.6 eV or the CF_2 peak at 292.0 eV. In curve fitting, the line width (full width at half-maximum, or fwhm) for the Gaussian peaks was maintained constant for all components in a particular spectrum. Surface elemental stoichiometries were determined from peak-area ratios, after correcting with the experimentally determined sensitivity factors, and were reliable to $\pm 5\%$. The elemental sensitivity factors were determined using stable binary compounds of well-established stoichiometries.

The ToF-SIMS analyses were carried out on an ION-TOF SIMS IV instrument (ION-TOF, GmbH, Münster, Germany). The primary ion beam (10 keV Ar^+) with a spot size of $\sim 50 \mu\text{m}$ was rastered over an area of $500 \mu\text{m} \times 500 \mu\text{m}$ while keeping the total dose under 10^{13} ions/ cm^2 . The pressure in the analysis chamber was maintained at 1.0×10^{-9} Torr or lower during each measurement. To reduce the charging effect, an electron flood gun was used for the charge neutralization. The calibration of the mass spectra was based on the built-in mass library.

The surface topography was studied by atomic force microscopy (AFM), using a Nanoscope IIIa AFM from Digital Instruments Inc. of Santa Barbara, CA. All images were obtained in the air using the tapping mode under a constant force (scan size, $10 \mu\text{m} \times 10 \mu\text{m}$; set point, 3.34 μV ; scan rate, 1.0 Hz). The film thickness was determined using an Alpha-STEP 500 Surface Profiler of KLA-Tencor Co., San Jose, CA.

FTIR Spectroscopy. The samples for the FTIR spectroscopy measurements were obtained by scraping the sputter-deposited fluoropolymer films from the Si substrates for dispersing in KBr pellets. The spectra were recorded in air on a Bio-Rad FT-IR, model 400, spectrophotometer. Each spectrum was collected by cumulating 30 scans at a resolution of 8 cm^{-1} .

Water Contact Angle Measurements. Static water contact angles of the pristine FEP film and the sputter-deposited fluoropolymer films on the Si(100) surfaces were measured by the sessile drop method at 25°C and 65% relative humidity using a contact angle goniometer (model 100-00-(230)), manufactured by the Rame-Hart, Inc. of Mountain Lakes, NJ. The telescope with a magnification power of 23 \times was equipped with a protractor of 1° graduation. For each contact angle reported, readings from five different locations on the film surface were averaged. Each angle reported was reliable to $\pm 3^\circ$.

Dielectric Constant Measurements. Samples for dielectric constant measurements were prepared by sputtering deposition of the fluoropolymer films on 150 mm (diameter) Si(100) wafers. Dielectric constant measurements were carried out on an SSM Mercury Probe CV system (model SSM 495) of Solid State Measurements, Inc., Pittsburgh, PA under a frequency of 100 kHz.

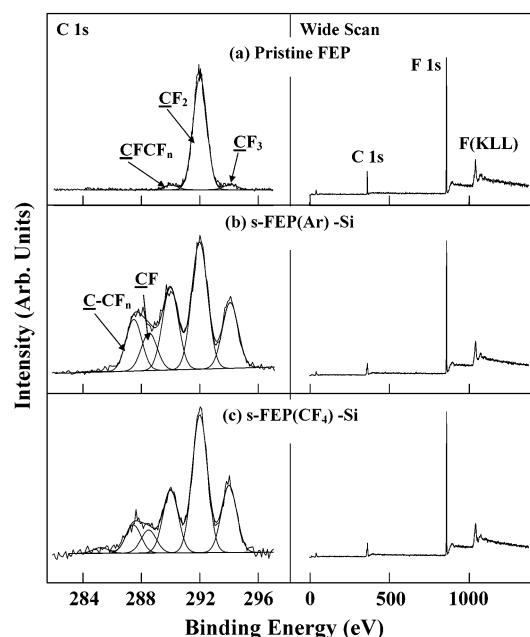


Figure 1. XPS C 1s and wide scan spectra of (a) the pristine FEP film, (b) the s-FEP(Ar)-Si surface, and (c) the s-FEP(CF₄)-Si surface.

Adhesion Strength Measurements. The adhesion strength of the sputter-deposited films to the Si(100) and GaAs(100) substrates was evaluated by the 180°-peel adhesion test. A copper foil adhesive tape was applied to the deposited fluoropolymer film on the substrate and subsequently peeled off on an Instron 5544 tensile tester from the Instron Corporation of Canton, MA. All peel tests were carried out at a cross-head speed of 10 mm/min. The copper foil adhesive tape was the product of Electron Microscopy Science Inc. of Fort Washington, PA. Each adhesion strength reported was the average of at least three sample measurements. The adhesion strengths among these measurements usually did not vary by more than ± 0.5 N/cm.

Results and Discussion

1. Chemical Composition of the Sputter-Deposited Fluoropolymer Films on Si(100) Surfaces. Figure 1a shows the C 1s core level and wide scan spectra of the pristine FEP film. The corresponding spectra of the sputter-deposited fluoropolymer films (the s-FEP films) on the preactivated Si(100) surfaces, using Ar and CF₄ as the sputtering gas, are shown in Figure 1, parts b and c, respectively. The Si surfaces so obtained are referred to as the s-FEP(Ar)-Si and the s-FEP(CF₄)-Si surfaces, respectively. The C 1s core-level spectrum of the pristine FEP film surface can be curve-fitted with three peak components having binding energies (BEs) at about 290.0, 292.0, and 294.1 eV, attributable to the CF-CF_n species, the CF₂ species, and the CF₃ species, respectively.¹⁹ The C 1s core-level spectrum of the s-FEP(Ar)-Si surface can be curve-fitted with five peak components, with BEs at 287.5 eV for the C-CF_n species, at 288.6 eV for the CF species, at 290.0 eV for the CF-CF_n species, at 292.0 eV for the CF₂ species, and at 294.1 eV for the CF₃ species.^{15,19,31,32} The C 1s core-level line shape of the s-FEP(CF₄)-Si surface (Figure 1c) resembles that of the s-FEP(Ar)-Si surface. The wide scan spectra of both surfaces, in turn, resemble that of the pristine FEP surface and consist of only the carbon and the fluorine signals. No oxygen species was discernible even after the air exposure. This result suggests that the residual free radicals in the s-FEP(Ar) and s-FEP(CF₄)

films have been annihilated during the aging process of the films in the vacuum chamber.

The relative proportions of the various fluorocarbon species in the C 1s core-level spectra of the pristine FEP surface, the s-FEP(Ar)-Si surface, and the s-FEP(CF₄)-Si surface are summarized in Table 1. The CF₂ species is the dominant species in the Ar plasma sputter-deposited fluoropolymer film. However, in comparison with the surface composition of the FEP film, the CF₂ concentration has decreased to a large extent. Correspondingly, two new species, viz., the CF and C-CF species, which are related to the cross-linked, branched, and/or the unsaturated structures, have appeared. The concentration of the CF₃ species, attributable to the terminal groups of the main chains and branches, has also increased. The [F]/[C] ratios for the pristine FEP surface, the s-FEP(Ar)-Si surface, and the s-FEP(CF₄)-Si surface, as calculated from their respective F 1s and C 1s core-level spectral peak area ratios, are also shown in Table 1. The Ar plasma sputter-deposited film is deficient in fluorine in comparison with the fluoropolymer target. The result is similar to that of the Ar plasma sputter-deposited PTFE film³⁰ and appears to be a common phenomenon found in the sputter-deposited fluorocarbon films.

The effect of other plasma gases, such as N₂, H₂, and O₂, on the chemical composition of the deposited fluoropolymer films was also investigated briefly. The resulting Si(100) surfaces with the sputter-deposited fluoropolymer films using N₂, H₂, and O₂ as the RF sputtering gas are referred to, respectively, as the s-FEP(N₂)-Si, the s-FEP(H₂)-Si, and the s-FEP(O₂)-Si surfaces. The [F]/[C] ratios and the relative proportions of the various fluorinated carbon species in the C 1s core-level spectra of these surfaces are also summarized in Table 1. Sputtering of FEP by CF₄ plasma produces a film with the highest proportion of the CF₂ (42.5%) and CF₃ species (20.5%), among all of the films deposited. This result is consistent with the highest [F]/[C] ratio observed for the s-FEP(CF₄)-Si surface. The s-FEP(CF₄)-Si surface, nevertheless, consists of similar fluorocarbon species as those of the s-FEP(Ar)-Si surface. Some N-containing species were incorporated into the N₂ plasma sputter-deposited fluoropolymer network. On the other hand, the H₂ plasma gives rise to extensive defluorination of the sputtered FEP fragments, similar to the case of the H₂ plasma treatment of the FEP surface.³³ The O₂ plasma fails to give rise to any significant amount of fluoropolymer deposit, because of the simultaneous etching effect of the O₂ plasma. Except in the case of the H₂ plasma sputter-deposited film, the CF₂ species is the most prominent species in the fluoropolymer films sputter-deposited from the FEP target under the present experimental conditions. Depending on the sputtering conditions, either the CF species³⁰ or the CF₂ species¹⁹ has been reported to be the dominant species in the sputter-deposited PTFE films.

The static water contact angles of the various Si(100) surfaces with the sputter-deposited fluoropolymer films are also listed in Table 1. The s-FEP(CF₄)-Si surface has the largest water contact angle, which is consistent with the fact that the surface has the highest [F]/[C] ratio, as well as the highest CF₃ group concentration. The high CF₃ concentration increases the surface density and thus the hydrophobicity of the surface.³⁴ The water contact angles of the s-FEP(Ar)-Si and the s-FEP(N₂)-Si surfaces are slightly lower than that of the pristine FEP surface. The water contact angle of the s-FEP(H₂)-Si surface is only about 77°. The decrease in contact angle (or hydrophobicity) of this surface is attributable to the presence of O-containing polar groups in its molecular structure. On the other hand, a small amount of carbonaceous material was deposited on the silicon

TABLE 1: Composition and Characteristics of the Pristine FEP and the s-FEP-Si Surfaces

| surfaces | [F]/[C] ratio | Composition | | | | | | | | | | | Characteristics | | |
|----------------------------|------------------|-------------|------|-----|-----|-------------------|-----|-------------------|-------------------|-----------------|---------------------------------|-----------------|-----------------------------|-------------------------|------------------------|
| | | CC | CO | C=O | COO | C-CF _n | CF | CFCF _n | CFNF ₂ | CF ₂ | CF ₂ NF ₂ | CF ₃ | deposition rate (nm/min) | contact angle (± 3°) | dielectric constant |
| pristine FEP | 2.0 | | | | | | | 3.8 | | 92 | | 4.2 | | 112 | 2.0 |
| s-FEP(Ar)-Si | 1.5 | 0.3 | | | | 14.1 | 0.3 | 22.6 | | 34.7 | | 18 | 5 | 109 | 2.0 ± 0.1 |
| s-FEP(CF ₄)-Si | 1.9 | 0.8 | | | | 9.2 | 6.9 | 19.3 | | 42.5 | | 20.5 | 2.2 | 116 | 2.1 ± 0.1 |
| s-FEP(N ₂)-Si | 1.6 | 1.6 | | | | 4.8 | 9.4 | 17.5 | 12.2 | 27.7 | 10.9 | 15.9 | 4.1 | 107 | |
| s-FEP(H ₂)-Si | 0.2 | 73.6 | 14.4 | 5.3 | 2.2 | | 2.6 | | | 1.8 | | | 1.4 | 77 | |
| s-FEP(O ₂)-Si | 0.2 | 84.3 | 9.5 | | 6.2 | | | | | | | | | 47 | |

surface arising from O₂ plasma sputtering, as show by the XPS data in Table 1. Thus, the water contact angle of the s-FEP(O₂)-Si surface increases to 47°, from about 20° for the pristine Si(100) surface.

Table 1 also shows the effect of the sputtering gas on the deposition rate of the fluoropolymer film on the Si(100) surface. Among all of the gases used, the Ar plasma gives rise to the highest deposition rate, whereas the H₂ plasma gives rise to the lowest deposition rate. In the case of the hydrogen plasma, the strong defluorination effect of the H₂ plasma reduces the deposition rate. The O₂ plasma fails to give rise to any significant deposition. It was reported that the deposited film was simultaneously etched by ion bombardment in the oxygen glow discharge.³⁵ A lower deposition rate in the case of CF₄ plasma suggests that such an etching effect is also present in the CF₄ glow discharge. A decrease in deposition rate has also been reported for the sputter-deposited polymer film from a mixed Ar-CF₄ plasma.³⁶ Thus, although the CF₄ gas plasma produces a film with a larger contact angle and a higher [F]/[C] ratio than those of the film produced by the Ar gas plasma, it was not used for the subsequent sputtering-deposition of FEP on the GaAs surface. Furthermore, the etching effect of the CF₄ plasma can also cause an increase in the surface states of GaAs.²⁹

Although the [F]/[C] ratios of the s-FEP(CF₄) and s-FEP(Ar) films are lower than that of the pristine FEP, the dielectric constants (κ) of the s-FEP(CF₄) and s-FEP(Ar) films are 2.0 ± 0.1 and 2.1 ± 0.1, respectively. These values are comparable to that of the pristine FEP film (κ = 2.0³⁷) and that of the pristine PTFE film (κ = 2.0–2.1³⁸). This phenomenon is probably attributable to the presence of cross-linked and branched structure, and thus the amorphous nature, of the s-FEP(CF₄) and s-FEP(Ar) films.

2. Chemical Structure of the Sputter-Deposited Fluoropolymer Films on Si(100) Surfaces. Figure 2 shows the respective FTIR spectra of the pristine FEP film (part a) and the fluoropolymer films deposited using Ar (part b), CF₄ (part c), N₂ (part d), and H₂ (part e) as the sputtering gas plasma. The spectrum of the pristine FEP film shows the CF_x (x = 1–3) stretching modes at 1100–1400 cm⁻¹. The absorbance bands at 1405 and 1450 cm⁻¹ are assigned to the CF₂ symmetric and asymmetric stretching mode, respectively.

The most prominent feature in the spectra of all of the sputter-deposited films is the strong, broad absorbance band at about 1100–1400 cm⁻¹, attributable to an overlap of the CF_x (x = 1–3) stretching modes. The weaker absorption bands at 740 and 990 cm⁻¹ correspond to the CF₃ vibration.^{39,40} The band at about 1720 cm⁻¹ is assigned to the -CF=CF- group, suggesting the formation of unsaturated structures in the deposited fluoropolymer films. This peak is shifted to 1750 cm⁻¹ for the N₂ plasma deposited film. The shift is probably caused by the incorporation of nitrogen into the deposited polymer chains.¹³ The FTIR spectrum of the N₂ plasma sputter-deposited film also shows an additional adsorption band at about 1340 cm⁻¹, which is normally attributable to the NO or COO group.⁴¹ However,

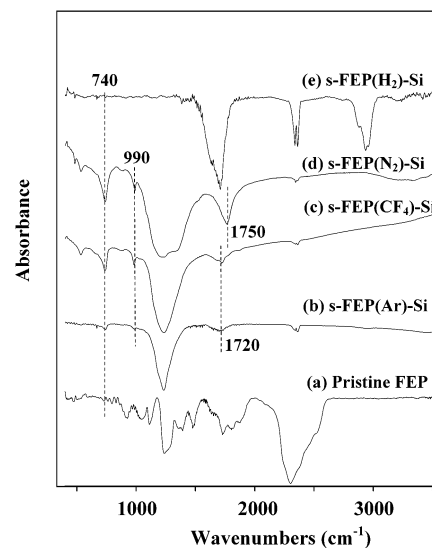
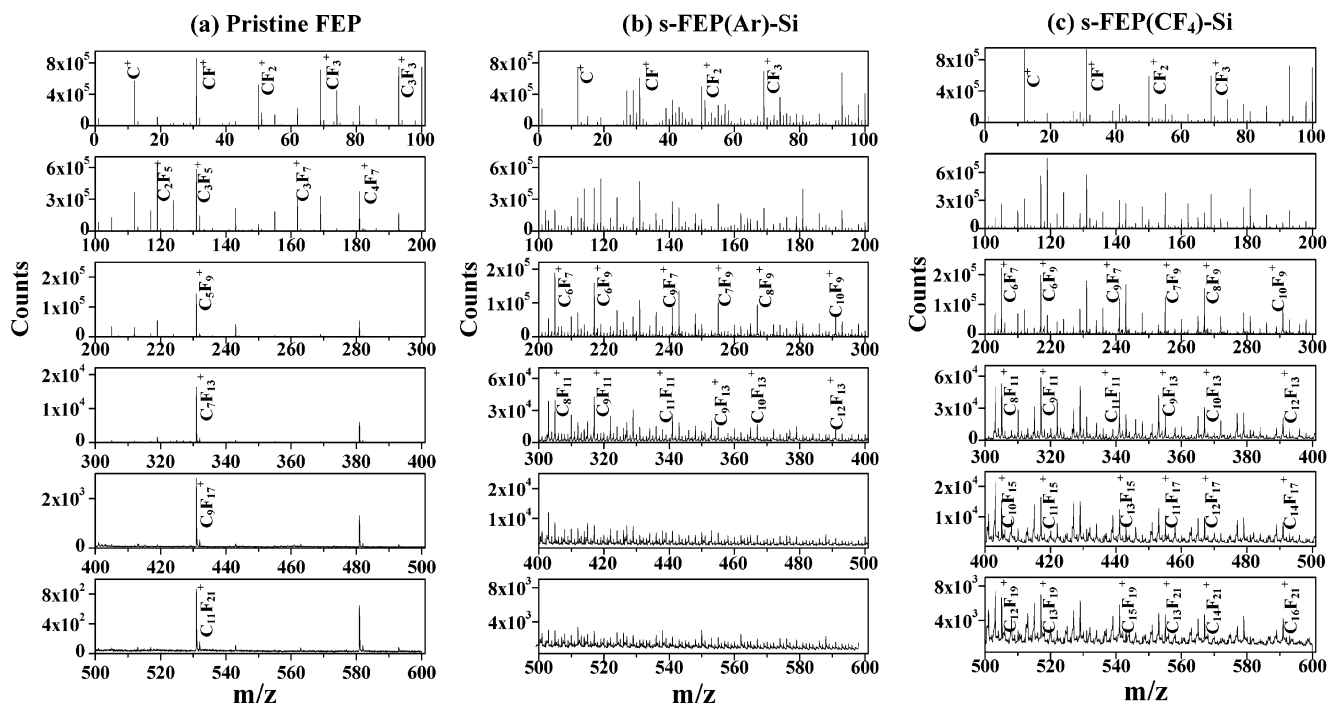


Figure 2. FTIR spectra of the sputtering-deposited FEP film using (a) Ar, (b) CF₄, (c) N₂, and (d) H₂ as the sputtering gas.

no oxygen species was detected in the deposited film by XPS. Thus, this absorption band is probably attributable to the CN group arising from the incorporation of nitrogen into the deposited polymer film.^{13,42} The s-FEP(H₂) film shows a characteristic absorption band for the CH group at 2800–3000 cm⁻¹ and a strong absorption band at about 1730 cm⁻¹ associated with the C=O group. The FTIR and the XPS results readily suggest that the s-FEP(H₂) film contains high concentrations of hydrocarbon and oxidized carbon species.

Figure 3 shows the positive ion ToF-SIMS spectra of the pristine FEP film (Figure 3a), the s-FEP(Ar)-Si surface (Figure 3b), and the s-FEP(CF₄)-Si surface (Figure 3c). The assignments of positive ions arising from the fractured segments of the pristine and sputter-deposited FEP polymer chains are shown in Scheme 1. The ToF-SIMS spectrum of the pristine FEP film contains peaks of the CF_x⁺ end groups with different FEP repeat units. On the other hand, the ToF-SIMS spectra of the sputter-deposited FEP polymers contain mass fragments of the FEP repeat units with different end groups, such as CF_x⁺, CF₃⁺, and C₂F₅⁺. The presence of FEP repeat units in the sputter-deposited films suggests that the s-FEP films contain -CF₂-CF(CF₃)- and -CF₂-CF₂-CF₂- segments, or oligomers, in their molecular chains. In addition, a number of fluorocarbon species are also observed in the ToF-SIMS spectra of the s-FEP films. The assignments of these positive ions are listed in Table 2. The presence of these fluorocarbon species suggests that the sputter-deposited FEP polymers are structurally disordered and cross-linked.

The XPS, FTIR, and ToF-SIMS results suggest that the sputter-deposited fluoropolymer films from the FEP target have long CF₂ segments with unsaturated, branched, and cross-linked structures. The RF sputtering of PTFE was understood to involve scission of the polymer chains to yield oligomeric segments,



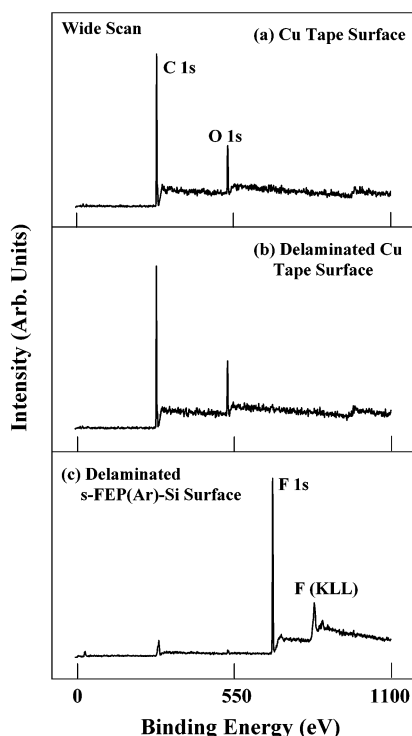


Figure 5. XPS wide scan spectra of (a) the Cu tape surface, and the delaminated (b) copper tape surface, and (c) s-FEP(Ar)–Si surface from a copper tape/s-FEP(Ar)–Si laminate having a 180°-peel adhesion of about 3 N/cm.

4. Adhesion of the Sputter-Deposited Fluoropolymer Films with the Si(100) and GaAs(100) Surfaces. The adhesion of polymeric dielectric materials to the silicon substrate is of great importance to the microelectronics industry. Generally, good adhesion is judged, qualitatively, by passing the Scotch tape peel test.¹ For the present work, the Scotch tape was replaced by the copper foil adhesive tape, because the latter exhibited an even better adhesion with the fluoropolymer films. The copper foil adhesive tapes were applied to the s-FEP(Ar)–Si and s-FEP(CF₄)–Si surfaces and subsequently peeled off on the tensile tester. The chemical composition of the delaminated fluoropolymer surface and the delaminated copper tape surface were analyzed by XPS. Figure 5 shows the respective wide scan spectra of the pristine copper tape surface, and the delaminated s-FEP(Ar)–Si and copper tape surfaces from a copper tape/s-FEP(Ar)–Si laminate having a 180°-peel adhesion strength of about 3 N/cm. The wide scan spectrum of the delaminated copper tape surface is similar to that of the original copper tape surface. On the other hand, the wide scan spectrum of the delaminated s-FEP(Ar)–Si surface is still dominated by the strong F 1s signal. These observations, as well as the absence of any fluorine signal in the wide scan spectrum of the delaminated copper tape surface, readily suggest that the copper tape/s-FEP(Ar)–Si assembly has delaminated by adhesional failure at the interface between the copper adhesive tape and the s-FEP(Ar)–Si substrate. Similar delamination results were observed for the copper tape with the Ar plasma sputter-deposited FEP film on the HCl-etched GaAs(100) surface. In this case, the fluoropolymer passivation layer (see below) remains intact on the GaAs surface after the copper tape peel test.

5. Passivation of GaAs(100) Surface by RF Sputtering Deposition of FEP Film. The hydrophobic nature and the good adhesion characteristics make the s-FEP film a potential candidate for the passivation of GaAs substrates. This applica-

tion would be in line with the fact that the ultrathin fluoropolymer films are also promising candidates for the dielectric barrier in a metal–insulator–GaAs device. Thus, attempts are made in the present work to passivate the GaAs(100) surfaces with the ultrathin s-FEP films deposited by Ar plasma sputtering.

Figure 6 shows the respective wide scan, As 3d, and Ga 3d core-level spectra of the pristine (as-received) GaAs(100) surface (Figure 6a) and the HCl-etched GaAs(100) surfaces after exposure to ambient air (~25 °C and 65% relative humidity) for about 0.1 h (time required to transfer the sample to the XPS chamber, Figure 6b) and 2 h (Figure 6c). The As 3d core-level spectrum of the pristine GaAs surface shows three spin–orbit-split doublets, having BEs at about 40.7 eV (3d_{5/2}) and 41.4 eV (3d_{3/2}) for the GaAs species, at about 44.0 eV (3d_{5/2}) and 44.7 eV (3d_{3/2}) for the As₂O₃ species, and at about 45.3 eV (3d_{5/2}) and 46.0 eV (3d_{3/2}) for the As₂O₅ species.²⁶ The Ga 3d core-level spectrum of the pristine GaAs surface, on the other hand, can be curve-fitted with two peak components, having BEs at 19.0 eV for the GaAs species and at 20.4 eV for the Ga₂O₃ species. The concentration of the As oxide species on the GaAs surface is defined as the As_xO_y/GaAs ratio and is derived from the ratio of the sum of the As₂O₃ and As₂O₅ spectral component areas to the GaAs component area. Similarly, the concentration of the Ga oxide species on the GaAs surface is defined as the Ga₂O₃/GaAs ratio. The initial As oxides and Ga oxides with concentrations as high as 0.38 and 0.68, respectively, are associated with the native oxides. The As and Ga oxides can be removed completely after treatment in concentrated HCl solution for about 2 min (Figure 6b). The O 1s peak component in the corresponding wide scan spectrum has disappeared almost completely after the HCl treatment. These results suggest that HCl treatment can effectively remove the native oxide layer on the GaAs(100) surface. However, the concentration of As and Ga oxides increases sharply after air exposure for 2 h (Figure 6c). In comparison with the spectra in Figure 6b, it can be observed that the proportion of the oxide species on the HCl-etched GaAs surface has increased substantially from negligible to about 0.25 in just 2 h of air exposure.

Figure 7 shows the respective XPS wide scan, As 3d core-level and Ga 3d core-level spectra of a HCl-etched GaAs(100) surface with the sputter-deposited s-FEP(Ar) film (the s-FEP(Ar)–GaAs surface) after exposure to ambient air for 50, 150, and 220 h. The sputter-deposition was carried out for about 80 s to give rise to an s-FEP film of about 6 nm in thickness. This thickness, which is less than the sampling depth of the XPS technique (~7.5 nm in a fluoropolymer matrix⁴⁴), allows the underlying GaAs surface to be studied by XPS. The As 3d core-level spectrum of the s-FEP–GaAs surfaces after 50 h of air exposure are dominated by a doublet, with a doublet splitting of 0.7 eV and a peak area ratio of 3:2, associated with the GaAs species. No apparent signals associated with the As or Ga oxides were discernible in both the As 3d and Ga 3d core-level spectra after 50 h of air exposure. Only a residual amount of As oxide was detected in the As 3d spectrum after 150 h of air exposure. The amount of the As oxide did not increase further after prolonging the air exposure to about 220 h, indicating that further oxidation was retarded. The XPS results thus suggest that the sputter-deposited ultrathin FEP film, with a thickness of less than 7.5 nm, can effectively retard the surface oxidation of the GaAs substrate under the atmospheric conditions. The effective barrier property of the ultrathin s-FEP film is probably attributable to the hydrophobic, cross-linked, and oxygen-free nature of the sputter-deposited fluoropolymer film. Thus, the feasibility of depositing stable and ultrathin barrier for moisture

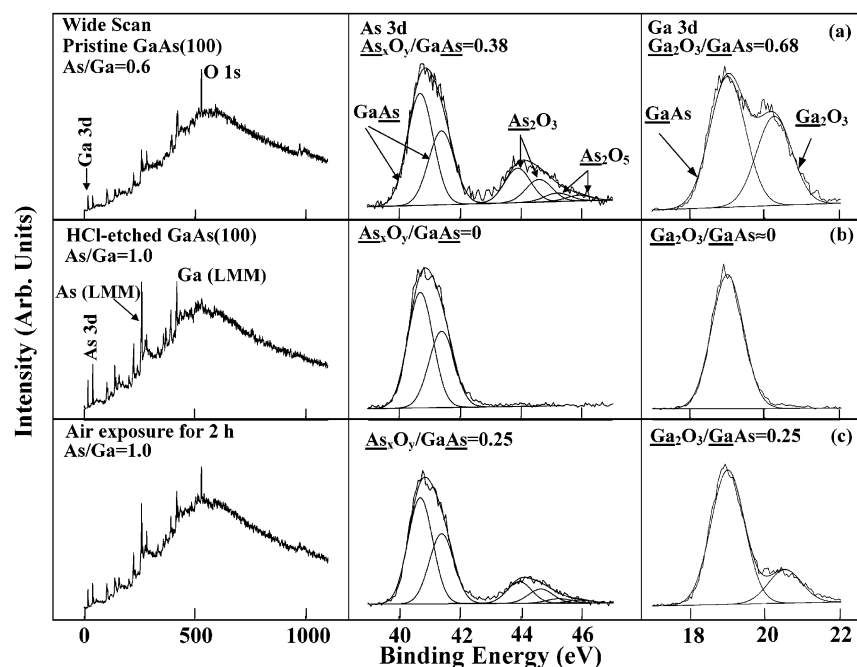


Figure 6. XPS wide scan spectra, and As 3d and Ga 3d core-level spectra of (a) the pristine GaAs surface, and the HCl-etched GaAs surface after exposure to air for (b) 0.1 and (c) 2 h.

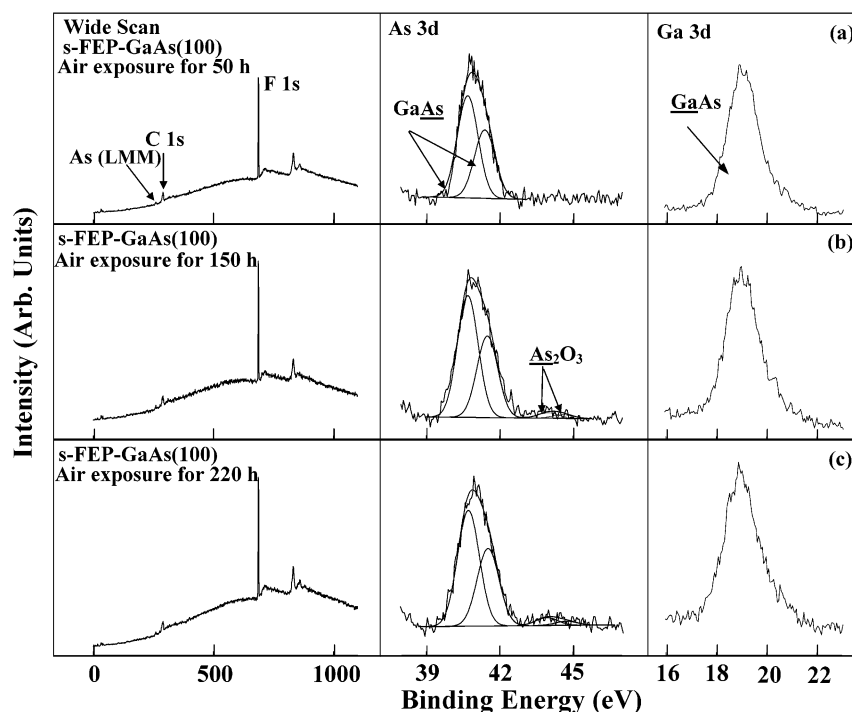


Figure 7. XPS wide scan spectra, and As 3d and Ga 3d core-level spectra of the s-FEP-GaAs surface after air exposure for (a) 50, (b) 150, and (c) 220 h.

and oxygen on the GaAs surface using the present RF sputtering technique is ascertained. Presumably, the barrier properties can be further improved (or perfected) by increasing the thickness of the fluoropolymer film to above 6 nm. However, a further increase in thickness of the fluoropolymer film will preclude the direct analysis of the underlying GaAs structure by the XPS technique.

Conclusion

Fluoropolymer films of 10–50 nm in thickness were deposited on the Si(100) substrates via plasma sputtering of an FEP

target in an RF magnetron sputtering system, using Ar, CF₄, N₂, H₂, and O₂ as the sputtering gas. The effects of the sputtering gas plasma on the chemical composition and structure of the sputter-deposited fluoropolymer films were investigated. The sputter-deposited fluoropolymer films contained long CF₂ segments, FEP repeat units, unsaturated bonds, and branched and cross-linked structures. The Ar plasma produced a fluoropolymer film with comparable water contact angle (surface hydrophobicity) and dielectric constant to those of the pristine FEP film. On the other hand, the surface of the HCl-etched GaAs(100) wafer could be effectively passivated by the Ar

plasma sputter-deposited FEP film of about 6 nm in thickness. The sputter-deposited FEP film with a dielectric constant of about 2.1 served as an effective oxygen and moisture barrier for the GaAs single-crystal substrate. The 180°-peel adhesion test results suggested that the sputter-deposited fluoropolymer films adhered strongly to the Si and GaAs substrates.

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