Polymer Vapour Deposition of Parylene-N and Parylene-C on Si(111)

Thin film characterization by FTIR and ellipsometry

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Parylene-N and parylene-C have been deposited from the gas phase on Si(111) via vapour deposition polymerization. Si(111) is widely used in electronic industry. The parylene film grew from the interior to the exterior therefore its thickness can be controlled in the range 100Å - 75µm. The thin film grew at a rate of 0.05µm/min. for parylene-C; the rate for parylene-N was lower. The process is solvent free and because the deposition takes place at room temperature, chemical, thermic, and mechanical stress are missing. The fringing effect is derived from the constructive and destructive interference of the IR beam from the parallel surfaces of parylene films. That indicates the high quality of the polymeric films, having smooth and parallel upper and bottom sides. The absence of the carbonyl (C=O) or carboxylic (C(=O)OH) bonds' vibrations suggest the good purity of the parylene films. The present work is a confirmation of the high quality parylene thin films that will be used for further experiments.

Keywords: Si(111), Parylene-N, Parylene-C, Polymer Vapour Deposition, FTIR

Parylene-N (fig. 1) is a dielectric with a low dissipation factor and a dielectric constant that is not dependent on the applied frequency. Parylene-C (fig.1) exhibits a high impermeability to moisture and corrosive environment and is the one being mostly used as isolator for the circuit boards. Parylene-N has a lower dissipation factor than parylene-C and penetrates better than parylene-C [1, 2]. Advantages of parylene coating are: a) uniform coating: thickness tolerances are typically held to +/- 20% from nominal; tolerances as tight as +/- 5% are possible when necessary; b) stability: parylene is inert and insoluble in most solvent systems within its useful range of temperature; parylene-C and parylene-N may be used up to 125°C continuously in the presence of oxygen; c) low stress process: polymerization of parylene takes place at room temperature; any object that can be exposed to medium vacuum can be parylene coated; d) optical clarity: parylene-C is optically clear while parylene-N exhibits a slight haze at thicknesses > 5µm [3]. The present work is a confirmation of the high quality parylene thin films that will be used for further experiments.

Experimental part
Sample preparation

Silicon (p-Si - B as dopant - double side polished, (5x21 mm²), thickness 300 µm ± 25 µm, orientation <111> ± 0.5º, resistivity 0.7-1.2 Ohm . cm) wafers were purchased from MTI Corporation, Richmond, CA 94804, USA.

Contaminants present on the surface of silicon wafers at the start of processing, or accumulated during processing, has to be removed in specific processing steps in order to get high performance / high reliability semiconductor devices. The RCA clean is the industry standard for removing contaminants from wafers developed by Werner Kern [4]. The RCA cleaning procedure has three steps used sequentially: a) organic clean: removal of insoluble organic contaminants with a 5:1:1 H₂O:H₂O₂:NH₄OH solution; b) oxide strip: removal of a thin silicon dioxide layer where metallic contaminants may accumulated as a result of (a), using a diluted 50:1 H₂O:HF solution; c) ionic clean: removal of ionic and heavy metal atomic contaminants using a solution of 6:1:1 H₂O:H₂O₂:HCl. The RCA cleaning technique does not attack silicon, and only a very thin layer of silicon dioxide is removed (in b) in the process. The procedure was also designed to prevent replating of metal contaminants from solution back to the wafer surface. When finished, the polished side should be specular with no residue [4].

Polymer vapour deposition

Parylene was deposited onto the Si(111) surface via vapour deposition polymerization from the gas phase. The deposition process has three phases: 1. dimer vaporization at 150°C; 2. dimer pyrolysis at 680°C when para-xyllyen is formed; 3. simultaneous adsorption and polymerization of the dimer onto Si(111) surface held around room temperature. A mechanical vacuum pump is pumping out the excess dimer. A schematic of parylene vapour deposition facility similar to the one we performed our deposition is presented in figure 2 [5].

Parylene deposition was performed in a Parylene Deposition System Model 2010 at a base pressure of 0.1 Torr at Metal Improvement Company LLC - Parylene Coating

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Services - Galway Division, Ireland. The geometry of the vacuum chamber allows the mounting of 3 Si(111) wafers of 4-inch in diameter each, or 1 Si(111) wafer of 6-inch diameter in one load. The deposition kinetics of parylene-N is lower than that of parylene-C; is proportional with the square root of the monomer concentration and proportional with 1/temperature \( T^{-1} \text{[K]} \). Prior to deposition any traces of oil / grease have been removed as previously described. The deposited parylene film covered conformally all the exposed surfaces. The process is solvent free and because deposition takes place at room temperature, chemical, thermic, and mechanical stress, is missing.

Thin films characterization was performed by ellipsometry and FTIR.

Ellipsometry

A Woollam V-VASE spectroscopic ellipsometer was employed to characterize the thin films. The measurements were done in the 200–1700 nm spectral range at different angles of incidence (AOI): 45, 60 and 75°, respectively. Here we present only the thickness measurement.

FTIR equipment and measuring conditions

Fourier Transform Infra-Red (FTIR) spectroscopy measurements were performed with a Perkin Elmer BX Spectrum spectrometer, in transmission mode. The spectra were recorded in the range 7800–380 cm\(^{-1}\), with a resolution of 4 cm\(^{-1}\) and a total of 150 scans per experiment.

Results and discussions

Polymer vapour deposition

The parylene film grew at a rate of 0.05 \( \mu \text{m/min.} \) (0.12 mil / h) for parylene-C; the rate for parylene-N was lower. After deposition the as-deposited Si(111) wafers have been checked followed by thickness measurement. Quality check was performed at Metal Improvement Company. It consist of mass spectrometry (MS) spectra (not presented here), temperature and pressure monitoring during deposition process, visual inspection of the thin film, adhesion studies and dielectric constant measurement (not presented here). The parylene film thickness deposited via polymer vapour deposition can be controlled with a precision of ±10% as opposed to the precision gained via conformal deposition from the liquid phase which is ±50% (both calculated with respect to the final thickness). The exact value of parylene thickness was determined by ellipsometry.

Ellipsometry

The parylene-N thin film has a thickness of approximately 3072 nm, while the parylene-C thick film is 3777 nm thick. The films thickness non-uniformity on the wafers is +/- 20 nm.

FTIR spectroscopy

The FTIR spectroscopy analyses were used to gather information about the functional groups present in the parylene films deposited onto Si (111) wafers, and to examine the chemical differences (new formation and/or degradation of chemical bonds) between the two polymers. Both Parylene-N/C and N/C-parylene represent the same chemical formula. Figure 3 displays the comparative FTIR spectra recorded for the parylene-N and parylene-C films. For a better visualization of all IR vibration bands the spectra are presented on three separate regions: 3200–2000 cm\(^{-1}\) (fig. 4a), 2000–1250 cm\(^{-1}\) (fig. 4b), and 1250–400 cm\(^{-1}\) (fig. 4c). No IR bands have been emphasized at lower wavelengths.
In the 3000–2700 cm\(^{-1}\) region emerge the absorption bands due to the symmetric and asymmetric stretching vibrations of sp\(^3\) and sp\(^2\) C-H bonds; whilst the 3100–3000 cm\(^{-1}\) region corresponds to the stretching vibration of C-H bonds in arenes (aromatic hydrocarbons) (fig. 4a) [6-8]. In the IR spectrum of parylene-N, the shoulder at ~3090 cm\(^{-1}\) can be ascribed to the vibrations of two neighboring H atoms belonging to the vibrations of two neighboring H atoms bonded to the ring, shifted to 826 cm\(^{-1}\) in the case of parylene-N and parylene-C films. Bands profile modifications and peak disappearances are observed. This was to be expected, as C-parylene fabrication consists in the substitution of a chlorine atom for one of the aromatic hydrogen of the parylene-N monomer. The presence of the aromatic chlorine is also demonstrated by the band peaking at ~877 cm\(^{-1}\), typical to single hydrogen bonded to the ring (CH) which is neighboring chlorine and ethyl group (fig. 4c) [10, 11]. Another fingerprint of parylene-C is the sharp band at 822 cm\(^{-1}\) (in the case of parylene-N), belonging to the vibrations of two neighboring H atoms bonded to the ring, shifted to 826 cm\(^{-1}\) in the case of parylene-C films (fig. 4c). This behaviour is not singular; shifts downward or upward can also be signaled for the bands at: ~962 (benzene breathing), 1342 (CH\(_3\) symmetric bending), 1417 (C-C deformation), 1454 (CH\(_2\) rocking), and 1515 (C=C ring stretching) [8, 12]. The various shifts of the bands suggest the occurrence of a series of short-range order structural modifications. The broadening of vibration bands can be associated with a low local symmetry and high atomic disorder. The prominent vibration band at ~563 cm\(^{-1}\) (parylene-N) can be ascribed to the phenylene out-of-plane ring bending. In the 1200–1000 cm\(^{-1}\) region appeared vibrations corresponding to the in-plane deformations of the C-H bond in the ring. The presence of the stretching and rocking vibrations of Si-O-Si bonds, as overlapped bands, cannot be excluded. Importantly, one can note the absence of the carbonyl (-C(=O)) or carboxylic (-C(=O)OH) bonds’ vibrations, which suggest the good purity of the parylene films.

Coatings of surfaces at micronic or even nanometric scale [12] are nowadays produced by a variety of chemical or physical procedures, polymer vapour deposition being one of them.

Conclusions

Parylene-N and parylene-C were deposited from the gas phase on Si(111) via vapour deposition polymerization. The parylene films grew from the interior to the exterior therefore its thickness can be controlled in the range 100-75\(\mu\)m. The thin film grew at a rate of 0.05\(\mu\)m/min. for parylene-C; the rate for parylene-N was lower. The parylene-N thin film has a thickness of approximately 3072 nm, while the parylene-C thin film is 3777 nm thick. The films’ thickness non-uniformity on the wafers is +/- 20 nm.

The appearance of the fringing effect indicates the high quality of the polymeric films, having smooth and parallel upper and bottom sides. The absence of the carbonyl (-C(=O)) or carboxylic (-C(=O)OH) bonds’ vibrations, which suggest the good purity of the parylene films.

References

1. *** http://www.scscookson.com/parylene/properties.cfm
2. *** Typical Properties of Parylene – Data sheet, Coating Metal Improvement Company, Galway, Ireland
3. *** The Coating Process – Data sheet, Parylene Coating Services, Katy, Texas, USA
12. CETINKAYA, M., BODUROGLU, S., DEMIREL, M.C., Polymer 48, 2007, p. 4130-4134

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