

Texture of vapor deposited parylene thin films

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The texture of vapor deposited parylene (poly-*p*-xylylene) thin films on Si is measured using the x-ray pole figure technique to quantify the crystalline portion. The as-deposited sample is the monoclinic α phase where the (020) fiber texture component comprises 48% and the remaining 52% are randomly oriented crystallites. The sample annealed for 350 °C 12 h is hexagonal β phase with an (040) fiber texture component of 68%. The half-width (ω) of the (040) fiber component of the β crystallites is within 25° of the substrate normal (fiber axis). In a β (040) oriented crystallite, the polymer chain is parallel to the Si substrate. This β fiber texture develops by polymer chain movement and rearrangement of the as-deposited α fiber texture.

Parylene (poly-*p*-xylylene) is a very low dielectric constant ($\epsilon=2.65$) vapor depositable semicrystalline polymer with a melting/dissociation temperature of 420 °C in N₂. Its potential application as an interlayer dielectric in high speed integrated circuits has recently been studied.^{1,2} The directional dependence of the dielectric constant may depend on the symmetry and the arrangement of the polymer chains/crystallites in the film so a detailed understanding of the crystallite structure of parylene thin films is needed, which includes crystallite orientation and polymer chain packing within the crystallites. Using the transmission electron/x-ray diffraction techniques, Niegisch qualitatively studied the molecular orientation in free standing parylene films.³ However, these techniques are very difficult to apply to thin polymer film deposited on a substrate. In this letter, we report on the use of the x-ray pole figure technique to quantify the texture of as-deposited and annealed parylene films on a Si substrate. The x-ray pole figure plots are interpreted to determine parylene molecular orientations within the crystallites along with the distributions of the oriented polymer crystallites.

Two crystalline phases are observed in bulk parylene, the α and the β phases. The α phase has a monoclinic crystal where the unit cell measures: $a=5.92$ Å, $b=10.64$ Å, $c=6.55$ Å, $\beta=134.7^\circ$.⁴ The β phase is hexagonal with $a=20.52$ Å, $c=6.55$ Å.^{5,6} The stable crystalline phase depends on the deposition conditions, particularly on the deposition temperature. When deposited at room temperature, the parylene film usually exists in the α phase with about 60% crystallinity.^{7,8} However, the α phase transforms to the more stable β phase above 220 °C, with the crystallinity increasing to 80%.⁵ Thus, substantial crystallinity is expected in the films for this study.

The parylene samples were vapor deposited at room temperature in a NovaTran parylene deposition system (model 1050) by a process first developed in 1966.⁹ The thickness of these parylene films is between 0.5 and 10 μm . The substrates are 75 mm Si(111) wafers. Selected samples were annealed in vacuum, with a base vacuum of 3×10^{-5} Pa

(10^{-4} Pa during annealing). Samples were annealed at 200 °C/30 min, 300 °C/2.5 h, and 350 °C/12 h.

Previously,^{2,10} it was determined that the as-deposited sample and the sample annealed below 200 °C have a Bragg diffraction peak around 16.6°, which implies an interplanar d spacing of 5.3 Å corresponding to the α (020). As the annealing temperature exceeds 250 °C, most α phase crystallites transform to β phase crystallites, with a prominent Bragg diffraction peak around 20.5°, which corresponds to an interplanar spacing of 4.4 Å. This crystal plane is the β (040) in the hexagonal unit cell which is parallel to the Si substrate.

A Siemens pole figure diffractometer was used to study the texture of thin parylene films. A schematic of the Schultz reflection geometry for an ideally oriented crystallite is shown in Fig. 1.¹¹⁻¹³ The experimental diffraction intensity data were background subtracted and corrected for both geometric defocusing and absorption using standard techniques.^{11,14,15} An equal area integration normalizes intensity values to a basis where random=1.

The pole figure data of parylene films indicates axial sample symmetry (no intensity variation with ϕ in Fig. 1) and, thus, a fiber texture.¹² The fiber axis corresponds to the Si substrate normal. It must be noted, however, that this fiber axis should not be misinterpreted as the polymer chain direction in the parylene/Si case. Because of the axial symmetry, the pole figure data are more directly represented as the fiber texture plots, with the β (040) intensity versus sample tilt

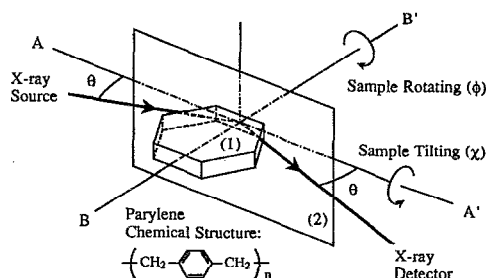


FIG. 1. The diffraction geometry for the x-ray pole figure measurement is shown for the β parylene film on a Si substrate (2). Parylene chemical structure is also shown. The β crystallite (1) is in an ideal orientation corresponds to $\chi=0^\circ$ in Fig. 2.

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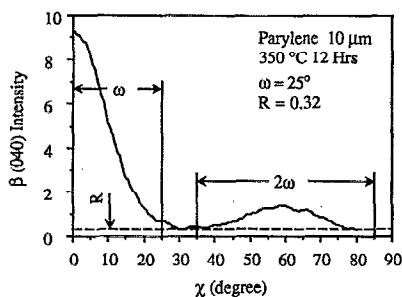


FIG. 2. The fiber texture plot of a β parylene sample annealed in vacuum at 350 °C for 12 h. The fiber axis is parallel to the substrate normal.

angle χ . A fiber texture plot in Fig. 2 shows a parylene film (10 μm thick) annealed in vacuum at 350 °C for 12 h.

The process of chain alignment and crystallization of the β phase parylene does not result in ideal crystallite alignment or a unique crystallite orientation as shown by the distribution of crystallite orientations with χ in Fig. 2. The spread about the fiber axis is given in Fig. 3 by ω , the half-width of the $\beta(040)$ distribution. In this β phase sample $\omega \sim 25^\circ$. The intensity distribution about $\chi=0^\circ$ is complemented by the band about $\chi=60^\circ$ due to the two additional members of the (040) family at $\pm 60^\circ$ as seen in Fig. 3. The axial symmetry and spread ω generate the peak at $\chi=60^\circ$ with the distribution width of 2ω on the fiber texture plot Fig. 2.

The $\beta(040)$ distribution does not decrease to zero outside the fiber component. Instead, the fiber texture component is superimposed on the random component, R , as shown in Fig. 2. By equal area integration of this background component, 32% of the crystallites are found to be randomly distributed. A similar procedure quantifies the (040) fiber component in the parylene film as 68%. In summary, this sample of β phase parylene has two components in the crystalline fraction: 68% of a (040) fiber with half-width of $\omega \sim 25^\circ$ and 32% random. The amorphous component, which is estimated

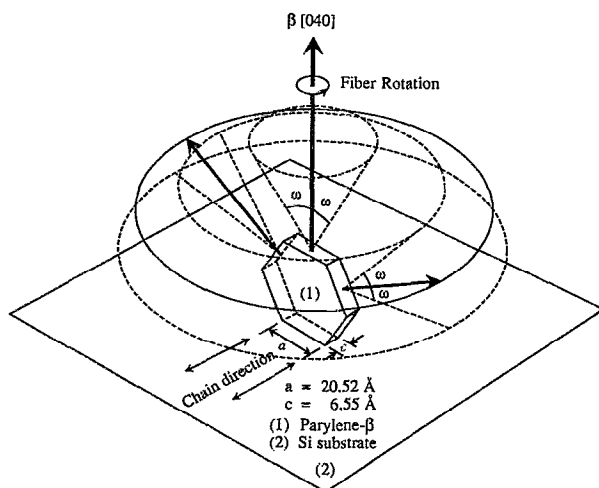


FIG. 3. A schematic illustration of the parylene/Si orientation relationship demonstrating the spread (ω) of the $\beta(040)$ distribution.

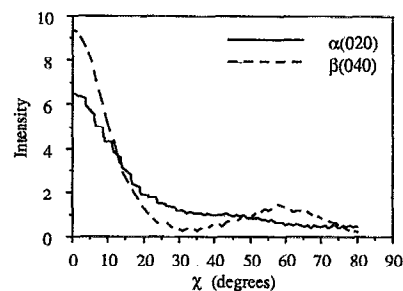


FIG. 4. The fiber texture plots of $\alpha(020)$ pole (solid line) and $\beta(040)$ (dash line). Both fiber axes are parallel to the substrate normal.

to be on the order of 20%,⁵ cannot be characterized by these x-ray diffraction techniques.

Although both α and β films have a fiber texture, the $\alpha(020)$ pole distribution in the as-deposited α phase parylene film differs from that of the $\beta(040)$ pole in the annealed β phase film. Figure 4 shows a fiber texture plot of an as-deposited α phase parylene film where the $\alpha(020)$ pole has a broader distribution ($\omega > 35^\circ$) than the $\beta(040)$ pole. Unlike the hexagonal $\beta(040)$, which has the multiplicity of six, the multiplicity of monoclinic $\alpha(020)$ is two, therefore, no corresponding peaks exist in the α phase film texture plot. The random component of α crystallites in the as-deposited film is 52%, while the (020) fiber component of 48% is much lower and broader (larger ω) than in the β phase. The fiber textures of other samples vary between the cases of the as-deposited and the 350 °C annealed samples, depending on the annealing conditions, as summarized in Table I.

To determine the molecular orientation in the polymer sample, one needs to know the relationship between the chain molecules and the unit cell, together with the relationship between the unit cell and Bragg planes.¹⁶ Since the parylene polymer chains in both α and β unit cells lie in the c direction,⁴⁻⁶ the molecular orientations in the parylene films are nominally parallel to the substrate plane [either $\alpha(020)$ or $\beta(040)$ planes] as shown in Fig. 3 for the β phase. Because the crystallites in both phases have a fiber texture, the parylene polymer chain directions in the films are azimuthally (ϕ) random from one crystallite to another. Even the most textured sample has the parylene $\beta(040)$ poles distributed within 25° of the fiber axis; therefore, parylene polymer chains in most crystallites are inclined relative to the substrate.

The crystallite and molecule orientations in parylene thin films result from the unique vapor deposition property of parylene. Because of the relatively higher deposition pres-

TABLE I. Parylene films' fiber texture as the function of annealing conditions.

Annealing temperature	Annealing time	Fiber component in parylene films	Spread of fiber component (ω)
as-deposited	...	48%	$>35^\circ$
200 °C	30 min	55%	35°
300 °C	2.5 h	61%	28°
350 °C	12 h	68%	25°

sure of parylene monomer (>1.3 Pa), as compared to the low pressure in metal vacuum vapor deposition ($<1.3 \times 10^{-3}$ Pa), the monomer molecules have high collision frequencies both in the vapor phase and with the substrate before polymerization on the substrate. The random collisions and the amorphous nature of the SiO_2 substrate surface result in an azimuthally (ϕ) random distribution of chain molecules and crystallite nuclei. The fiber texture is retained during the α to β phase transition because only a short range chain reorientation is involved. The crystallite distribution in the χ direction, however, changes with the phase transition as seen in Fig. 4. Two processes occur during the annealing treatment and phase transformation that sharpen the texture. Although the chain direction is unchanged in the crystallites, local rearrangement improves the crystallite alignment. Furthermore, the average crystallite size, estimated from x-ray line broadening, increases from ~ 100 Å in the as-deposited α phase to ~ 200 Å in the β phase after anneal. The texture data indicate that the randomly oriented crystallites are consumed by more rapidly growing oriented crystallites. The oriented β crystallites could also grow at the expense of the amorphous fraction, however, measurements were not made of the amorphous fraction to test this hypothesis.

In summary, we have demonstrated that the crystalline portion of parylene is textured by vapor deposition process. The x-ray pole figure technique is an effective method to quantify the texture. As-deposited and annealed parylene film consist of $\alpha(020)$ fiber+random texture and $\beta(040)$ fiber+random texture, respectively. The fiber component has

a distribution of orientations. Annealing results in an α to β phase transformation accompanied by crystallite growth which sharpens the texture, primarily by reducing the random fraction of crystallites.

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