Anisotropic pyrolytic carbon and the Volmer-Weber island growth mechanism – is the structure of the former a consequence of growth by the latter?

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The nature of pyrolytic carbon (Pyc) growth has been debated for over half a century, and yet no growth mechanism has been reported that adequately describes all the structural features observed\(^1\). The physical properties of Pyc based materials are well known to be dependent on the carbon structure, which itself is determined by the growth conditions\(^2\). Armed with an understanding of the growth mechanism it may be possible to produce Pyc with the physical properties desired for specific applications. In this report we propose that anisotropic Pyc forms by the Volmer-Weber island growth mechanism, and experimental and modeling results are provided to support this proposition. The potential to use this finding to influence the structure of the Pyc by control of the substrate surface is discussed.

Pyc constitutes an important class of carbon material and is employed in a wide range of industrial and consumer applications\(^1\). Pyc is generally grown by the pyrolysis of hydrocarbons, either on surfaces by chemical vapor deposition or in porous materials by chemical vapor infiltration\(^2\). Despite the industrial importance of Pyc materials, and the numerous studies reported on their structure, aspects of the growth mechanism remain elusive\(^1\). Pyc materials are generally classified as being optically isotropic or anisotropic, with the anisotropic form being the more attractive for most applications\(^2\). The relationship between the structure of Pyc and the growth conditions has been extensively studied, and a number of key factors have been recognized to influence the Pyc structure, including: the hydrocarbon precursor; pressure; temperature; and residence time\(^1\). The structure of Pyc has also been the focus numerous reports. The anisotropic form is of particular interest, being comprised of columnar structures (often described as “growth cones”) of various sizes that usually emanate from the substrate surface and appear as a lamella at the surface of the deposit producing a tessellated surface\(^3-5\).
In 1964 two reports, one by Coffin and the other by Sublet, Auriol and Rappeneau, proposed differing theories to account for the formation of these structures\textsuperscript{3,5}. An image of conical structures from the work of Sublet et al. is presented in Fig 1. Sublet proposed that the “growth cones” formed from spherical “germs” grew from the substrate surface, whereas Coffin rationalized the growth on the basis of layered deposition over surface asperity. To date, neither these, nor any new theories appear to have been generally accepted. The theory proposed by Coffin is inconsistent with aspects of the structure of Pyc, in particular it doesn’t explain the grain boundaries between columns, nor is it clear why all surface roughness (presumably with a range of different morphologies) would produce the same hyperboloid shaped columns. Despite apparent weaknesses in this theory it is still commonly invoked to explain the formation of the columnar structures\textsuperscript{2,6,7}. In contrast, the theory of Sublet appears to have been forgotten. One possible reason for this is that Sublet et al., although noting that surface roughness promoted the formation of larger “growth cones”, did not demonstrate why this was the case, and in fact stated that geometry was not sufficient to explain the appearance of large cones. While the theory proposed by Sublet has not been generally accepted, aspects of the theory have been verified in other studies. In particular, several studies of the initial stages of Pyc deposition have recently demonstrated that growth begins with the formation of isolated deposits that rapidly coalesce\textsuperscript{8-10}. Other studies have noted the presence of granular layers, often comprised of spherical structures, at substrate/Pyc interfaces\textsuperscript{7,10}. Despite these observations the theory of Sublet appears not to have been reconsidered. In this report we revisit and revise Sublet’s original theory. The growth of Pyc on a ZrO\textsubscript{2} surface is described, which appears to follow the Volmer-Weber 3D island (V-W) growth mechanism\textsuperscript{11}. We demonstrate how the columnar structures, characteristic of anisotropic Pyc are also consistent with the action of this mechanism and how “growth cones” are simply large columnar structures produced by the action of the V-W mechanism on surface asperity.
A reactor tube comprised of zirconia with 10.5% yttria was stacked with wafers of zirconia with 6% scandia (Ceramatec) and heated to 1673 K under a flow of argon\textsuperscript{12}. Once the temperature had stabilized methane (1%) and oxygen (CH\textsubscript{4}: O\textsubscript{2} = 1.1) were introduced into the feed (total flow = 5000 sccm) and this flow was maintained for a period of 240 minutes. During this time the product gas composition was analyzed periodically by gas chromatography (GC). After 240 minutes the reactive components were removed from the feed and the argon flow rate was reduced to 150 sccm. The reactor was cooled to ambient temperature and the wafers were removed for analysis.

The surfaces of the zirconia wafers were analyzed by scanning electron microscopy (SEM; FE-SEM Philips XL30 and FEI Helios Nanolab 600 FIB-SEM) combined with energy disperse X-ray (EDX) analysis and micro-Raman spectroscopy (Reinshaw Invia, \(\lambda_0 = 514.5\) nm).

SEM examination of the surface of the zirconia wafers showed the presence of carbon deposits that resembled Johnson-Mehl tessellations, with polygonal elements with triple-point grain boundaries (Fig. 2a). Some areas of the ZrO\textsubscript{2} surface were not covered by a continuous film, but rather by non-continuous carbon deposits, as shown in Fig. 2b and c. These deposits were either isolated carbon hemispheres or non-continuous Johnson-Mehl tessellations.

A number of isolated hemispherical deposits were sliced by FIB milling and the resulting cross-sections examined by SEM. One such cross-section is shown as an inset in Fig. 2c. The appearance of these cross-sections supported the assessment that the deposits were hemispheres, and EDX analysis showed that they were comprised of solid carbon. Because of the likelihood that the FIB milling technique had changed the internal structure of the deposits, the inside of a deposit that had been mechanically damaged was examined and
found to be comprised of concentric layers of carbon (Supplementary Information - Fig. S1). The nature of the carbon structure was examined using micro-Raman spectroscopy. From the Raman spectra the $I_D/I_G$ ratio was found to be ca. 1.59, consistent with graphite with a low degree of order.

These observations are consistent with growth by the V-W mechanism. For this mechanism, which is well known in epitaxial thin film growth, nucleation on a surface leads to islands that on growing further impinge upon one another and eventually coalesce into a continuous film\textsuperscript{13}. Growth via this mechanism has been well described with mathematical models\textsuperscript{14}, however, for our purposes a simple model was developed to investigate the consequences of this mechanism on the structure of Pyc materials. The model seeds nuclei randomly on a flat surface at a constant rate per unit area. Once a nucleus is generated it grows at a constant radial growth velocity in free (non-occupied) directions. Seed points accumulate only on the substrate. A time sequence generated using this model is presented in Fig. 3.

This model generates all characteristic morphological features of the deposits observed. In this study the Pyc growth was interrupted prior to coalescence of the hemispherical islands due to a relatively low nucleation density and a slow rate of growth. We postulated that growth by the V-W mechanisms may be common, but the initial stages seldom seen due to higher densities of nucleation sites resulting in rapid film formation. The model was used to investigate this by increasing the nucleation site density by ca. 1000. Under these conditions rapid coverage of the substrate surface indeed occurred (Fig. 4). In addition, with the higher nucleation density the effect of the growth mechanism on the structure of the material also becomes apparent. From the cross-section in Fig. 4c, it is clear that the structure is columnar. This is consistent with numerous experimental reports of the structure of anisotropic Pyc\textsuperscript{3,6,7,15-18}. 
It can also be seen that the number of elements in the tessellation reduces with film growth. This is a consequence of the constant rate of nucleation. For any two neighboring columns the column that originated for the earliest seeded nuclei impinges on the column seeded later. Consequently, columns based on the earliest forming nuclei progressively dominate the structure with time by terminating the growth of columns seeded later. This is most obvious in the early stages of growth where the cross-sectional structure of the deposit looks somewhat disordered due to the rapid termination of columns originating from the latest formed nuclei (see the cross-section in Fig. 4b).

The presence of grain boundaries between adjacent columns appears to be a consequence of V-W growth and the nature of graphitic layers. When two growing hemispheres meet their graphitic planes will be misaligned. Consequently the graphitic layers will not merge to form a continuous structure. This behavior clearly continues throughout the growth process, even as the graphitic planes between adjacent columns become more closely aligned.

Another structural feature of anisotropic Pyc often described in the literature is the presence of hyperboloid structures that result from surface asperity. The simple model of V-W growth was applied to surfaces with surface roughness and the results are shown in Fig. 5.

From Fig. 5 the V-W growth over surface asperity can clearly form hyperboloid structures similar to those reported. In contrast to Coffin’s theory, that proposed that the hyperboloid structures form as a consequence of layered growth over substrate asperity, the structures instead form due to V-W growth from nuclei formed above the substrate surface. The columns formed from these nuclei have a similar advantage to those that are formed earlier (vide supra). During the growth of the film they impinge on the neighboring columns of nuclei formed lower, resulting in the hyperboloid structures formed. The higher above the
substrate a nuclei is formed the more privileged is its resulting column. Although appearing as hyperboloids in cross-section these structures are not true hyperboloids as they are comprised of a number of planes at the intersection of adjacent columns. This is apparent when the surface is viewed from above, as the surface of the column is polygonal rather than circular.

An important consequence of the V-W mechanism is that surface roughness will have a significant effect on the structure of the growth columns formed. Fig. 5c shows the result of growth over a surface with periodic roughness. In this scenario the columns formed from higher nuclei are less privileged than the example of a single protrusion. This results fewer growth columns at the surface than the case of no substrate roughness (Fig. 5a), and columns with a smaller cross-sectional area that the large hyperboloid column formed in the case of a single protrusion (Fig. 5b).

With an understanding of the role of the V-W growth in anisotropic PyC formation it is possible to identify the factors that will control the texture at the surface of a PyC material. Four factors will control the cross-sectional area of lamella at the surface of growth cones: the density of nucleation sites; the rate of nucleation; the thickness of the PyC layer; and the nucleation site height distribution. The first two of these factors will be determined by the nature of the substrate and the gas-phase growth conditions, the third by the rate and duration of growth, and the fourth by the substrate surface. By use of models that describe the V-W growth mechanism it will be possible to design surfaces that, in combination with control of other growth factors, will enable PyC with the desired structure, and hence physical properties, to be produced.

To conclude, it is perhaps important to note that the mechanisms of Coffin and Sublet are both valid. Coffin’s mechanism is certainly correct when applied on a macro-scale, and is in
fact a type of patterning. Sublet’s theory is in essence correct, erring only in describing the “seeds” as spherical and in interpreting the effect of surface roughness.

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Author contributions

JP, NB, WJL and CL designed the experiments. WJL and CL conducted the experiments. JP and JG designed and conducted the modeling study. JP, WJL and JG interpreted the results of the experiments and modeling. JP wrote the paper.
Figures legends

Fig. 1. Columnar structures in the cross-section of a Pc deposit from the initial report of Sublet *et al.*\(^5\).
Fig. 2. SEM images of: (a) a carbon film on a zirconia surface; (b) non-continuous carbon deposits on zirconia view from above; (c) similar deposits as show in (b) but viewed at an angle of 40° to the zirconia surface (Inset - A SEM image of the cross-section of a hemispherical carbon deposit sliced by FIB milling).
Fig. 3. A schematic representation of a time sequence for growth by the V-W mechanism: (a) represents a stage at which most deposits are individual hemispherical islands; (b) represents a stage at which the hemispherical islands have begun to impinge and coalesce; (c) represents a stage shortly after all islands have coalesced and a continuous film has formed. Upper images represent the view from perpendicular to the ceramic surface and lower images represent a cross-section along the surface (A-A). Each shade of grey represents a carbon structure grown from an individual nucleus. Red represents the substrate and blue the vapor above.
Fig. 4. A schematic representation of a time sequence for growth by the V-W mechanism with a density of nuclei ca. 1000 times greater than that for Fig. 3: (a) represents a stage at which most deposits are individual hemispherical islands; (b) represents a time stage shortly after all islands have coalesced and a continuous film has formed; (c) represents a mature stage of growth at which the cones from nuclei formed early in the growth period have come to dominate the structure.
Fig. 5. A schematic representation of growth by the V-W mechanism over surfaces with different roughness at a mature stage of growth: (a) growth over a flat surface; (b) growth over a protrusion on a flat surface; (c) growth over multiple periodic protrusions each with the same height as the protrusion shown in (a).
Supplementary Information

Fig. S1. A SEM image of a mechanically damaged Pyc deposit.