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FRACTAL AND SPHERULITIC MORPHOLOGY OF SILICON NITRIDE CRYSTALLIZED FROM AMORPHOUS FILMS

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Abstract

Thin films of substoiciometric silicon nitride were grown by the use of ion beam assisted deposition. The amorphous films were annealed at high temperatures (1017-1200 °C) to produce crystalline alpha-Si_3N_4. Both highly symmetric spherulitic crystal morphologies and irregular fractal aggregates were seen. In the latter case, a fractal dimension of 1.2 was measured. These two macroscopically different forms possessed correspondingly different microstructures. The morphologies were found to be determined by the temperature of the anneal.

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When a non-equilibrium system results in the growth of crystalline aggregates a multitude of morphologies are possible.[1] Variations in the conditions at the growing interface are very important. The rate at which material arrives, its sticking probability and mobility at the growing interface, and the anisotropy of the system all contribute to the resulting crystalline morphology. With so many factors affecting the growing interface it is remarkable that a small number of crystalline forms are seen appearing in many seemingly disparate systems. These well known forms are dendrites, spherulites and fractal aggregates.

Dendrites appear in systems with large anisotropies and are characterized by having stable parabolic tips. They often display symmetry determined by the underlying anisotropy. Water and ammonium bromide can be made to crystalize in this form.[2] Spherulites, which have often been seen in two dimensional systems, are crystalline aggregates that are cylindrically symmetric and appear to have a nearly perfect circular perimeter. These morphologies are often seen in polymers[3] and glasses[4], and have been observed during annealing of $Al_{0.4}Ge_{0.6}$ and Se films.[5,6] Fractalline forms are often produced where the rate limiting step of solidification is the diffusion of the incorporated species. The formalism of this diffusion limited aggregation (DLA) was introduced by Witten and Sander[7]. These usually highly ramified patterns have been seen in sputter deposition of films[8], dielectric breakdown patterns[9] and crystallization of amorphous films.[10]

It has recently been reported that electrochemical deposition of zinc can result in more than one type of crystalline morphology.[11,12] By varying the parameters of the experiment, notably the applied voltage on the cell, it is possible to produce dendritic, spherulitic (also called dense radial aggregates) or DLA type growth. The present experiment similarly shows the ability to change the morphology of the crystallization by varying the conditions of the experiment. Silicon nitride can form aggregates in either a spherulitic or fractalline form. These two different macroscopic morphologies in addition possess correspondingly different microscopic structure.

Thin films of substoichiometric silicon nitride were deposited on silicon substrates using the ion beam assisted deposition technique. The apparatus used in the experiment has been described in greater detail in previous publications, so only a brief description will be offered here.[13] The composition of the films was determined by varying the ratio of the silicon particle flux from an electron beam evaporator to the amount of nitrogen implanted into the film from a 500 eV ion gun. The energy of the nitrogen ions caused collision cascades in the growing material, which resulted in a highly dense, pure amorphous film. Before deposition the (111) and (100) oriented silicon substrates were sputter cleaned with nitrogen. This procedure also made the surface layer amorphous, which would tend to ameliorate any anisotropic effects on the growing film caused by the substrate's crystallographic orientation.

Alloy films of composition $Si_3N_{2.8}$ with thickness 500 nm were deposited on (111) and (100) oriented silicon substrates. The compositions were determined by Rutherford Backscattering Spectrometry (RBS). Samples were then annealed in an argon atmosphere at 1200 °C for 45 minutes, which produced nucleation and growth of spherulitic crystalline aggregates of Si_3N_4 (Fig. 1). Changing the substrate's orientation did not affect the film's crystallization.

This morphology starts from a single nucleation site from which long, thin crystalline fingers grow as spokes from the hub of the wheel.[14] The individual fingers grow with a particular fast crystalline growth direction aligned along their length. The tips of the fingers are not stable however, and split periodically to maintain a constant distance between the branches.[5] The excess silicon in the film remains embedded in the spaces between the branches. Consequently, films with less excess silicon produce crystals with a much finer texture.[14] Scanning electron microscopy indicates that the thickness of the spherulites is the same as that of the film.

Because Si_3N_4 is a birefringent material, spherulites viewed with an optical polarizer and analyzer set at 90 degrees with respect to each other show a characteristic Maltese Cross pattern.[15] The vertical and horizontal black bands appear on the sample where the branches are aligned either with the polarizer or the analyzer. In other intermediate quadrants the birefringent property of the material rotates the polarization direction of the light which has already passed through the polarizer and allows it to also pass through the analyzer.

The most remarkable feature of the spherulites must be that their perimeter usually is nearly a perfect circle. Some mechanism, possibly involving the transport of the heat of crystallization along the fibers must operate to retard the growth of statistical fluctuations of the growing envelope. Further study will be necessary to apply theories such as those described by Greer et al. for electrochemical deposition.[16]

The microstructure of the spherulites was determined by θ-2θ X-ray diffraction (XRD) using Cu K-alpha X-ray, a curved graphite monocrometer and an 0.125 degree per minute scan rate. Spectra typically took eight hours to accumulate. The predominant X-ray peaks were of the hk0 variety regardless of substrate orientation. This confirmed the fact that the c-axis of the Si_3N_4 crystals lay in the plane of the surface, a necessary condition for the observed birefringence. In fact, careful optical studies have determined that the c-axis of the crystals was perpendicular to the growth direction of the branch and to the sample normal.[17]

Reducing the annealing temperature to 1017 °C produced a second crystalline morphology which was macroscopically and microscopically different from the spherulites. (Fig. 2) This Si_3N_4 aggregate appeared as an irregularly shaped cluster. Viewed between crossed polarizers the material was not nearly as bright as the spherulites and has a very fine grainy texture. These optical micrographs indicated that this second phase consisted of numerous small crystallites, oriented primarily in such a way as to reduce the observed birefringence. X-ray scattering data confirmed these assertions. Films grown on both (111) and (100) silicon substrates showed X-ray peaks for (200) (102) (210) (211) planes as well as disproportionately large scattering intensities for the (002) and (004) planes. Previous work had shown that the basal plane of silicon nitride is crystallographically favored to lie on the (111) silicon plane.[18] Since the first X-ray measurements were performed on films grown on (111) oriented silicon, it was originally thought that interaction with the substrate was causing preferential crystallization with the c-axis normal to the surface. Subsequent work using (100) oriented silicon shows the same behavior in the films and it now seems probable that the mechanism of crystallization was not strongly influenced by the substrate.

Unlike the very circular spherulites, these crystalline aggregates had a very rough and irregular boundary. Measurements indicated that the perimeters of these crystalline islands had a fractal dimension of approximately 1.2. According to the formalism of Mandelbrot, the length of the perimeter of any object can be measured by approximating the curve with a series of straight line segments of equal length.[19] The length of the perimeter is the product of the length of the segment and the number of segments used. As the size of the line segment is decreased, the perimeter length measure quickly approaches a single value if the perimeter is well defined. The dimension of the perimeter is therefore equal to unity. If the measured perimeter continues to grow as the length of the measuring segment decreases, the object is said to have a perimeter with a fractal dimension that is greater than unity. In Figure 3, the logarithm of the measured perimeter is plotted versus the logarithm of the measuring segment for one spherulite and three fractal aggregates. The slope of the best fit line through the data points is 1-Dp where Dp is the fractal dimension. (Here we use the symbol, Dp, denoting a fractal perimeter rather than a fractal area.) For the spherulite, Dp equals 1.01 ± 0.03 , indicating that the circular perimeter is well behaved. For five fractal aggregates measured, Dp equals 1.32 ± 0.02, 1.28 ± 0.02, 1.23 ± 0.02, 1.20 ± 0.02, and 1.15 ± 0.03.

It must be noted that the fractal dimension of any curve is defined only for a certain range of segment lengths. If the segment is of comparable size to the object, the perimeter will be underestimated. If the segment length is very small the position of the perimeter may not be defined sufficiently well for a measurement to be made.[19]

In many diffusion limited systems, aggregates form with ramified, randomly branched morphologies. It is possible to determine the fractal dimension (Da) of these objects in a form which reflects the ability of the aggregates to fill space.[8] In this method, concentric circles of varying radii are drawn, centered at the nucleus of the cluster. The logarithm of the total length of aggregate branches within each circle is plotted versus the logarithm of the radius of the circle. As before, the slope of the best fit line through the points equals 1-Da. Crystal morphologies in these two-dimensional systems have a fractal dimension (Da) less than their Euclidean dimension of two, indicating that they are not space filling. In the present system, the aggregates which form clearly are space filling, and so have a fractal dimension (Da) equal to the Euclidean dimension of the system, which is two. It is the perimeter which is fractal in nature, and is therefore different from its Euclidean dimension, which is unity.

Computer simulations of diffusion limited aggregation have been performed which produced ramified structures with fractal dimensions (Da) of approximately 1.7 and therefore do not accurately simulate the clusters in the present system.[7] Most of these studies, however, rely on two assumptions. First, the step size of the diffusing particles is fixed to the smallest length scale of the simulation. Second, the particle is required to stick to the growing aggregate the first time it reaches a site immediately adjacent to the cluster. If these two conditions are relaxed, it is possible to simulate the growth of aggregates which are nearly space filling (Da-2) and have perimeters at least qualitatively similar to those seen in the present system.[20,21] Work has begun to determine which parameters are required to simulate the type of clusters which are seen here. (Da-2, Dp-1.2)

In summary, a system has been presented in which there is a crossover between two different types of crystalline morphologies. At higher annealing temperatures, spherulitic growth is favored. At lower temperatures, a compact crystalline aggregate with an irregularly shaped perimeter is formed. This boundary is seen to have a fractal dimension of approximately 1.2.

Previous work has shown that Si_3N_4 crystallizes in nitrogen implanted silicon. Although irregularly shaped spherulites have been seen,[22] these crystals usually displayed dendritic growth, which is not seen in the present system.[23,18] In the present work, it is apparent that the crystalline anisotropy responsible for dendritic growth is not present in the amorphous silicon nitride films or in large enough amounts in the growing aggregate. Substrate preparation, previously mentioned, was sufficiently severe to make the substrate surface completely amorphous before deposition and even during the anneal served to disrupt whatever anisotropic effect the substrate might have had on the growing aggregate.

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Figure Captions

Fig. 1 Optical micrograph of spherulitic growth of Si_3N_4 taken with crossed polarizers. The sample was prepared by annealing a 500 nm thick amorphous film of $Si_3N_{2.8}$ at 1200 °C for 45 minutes.

Fig. 2 Optical micrograph of Si_3N_4 fractal aggregate. The sample was prepared by annealing a 500 nm thick amorphous film of $Si_3N_{2.8}$ at 1200 °C for 45 minutes to initiate nucleation and then at 1017 °C for 137 hours.

Fig. 3 For three fractal aggregates and one spherulite the $\log_{10}$(Perimeter length in mm*430) vs. $\log_{10}$(Segment length in mm*430) is shown. The data from the spherulite is presented as solid circles with error bars at each point where the error is larger than the size of the symbol. The linear least squares fit to each data set is shown. The slopes (m) of the lines are indicated. The two spherulite data points at the extreme right were not included in the fit.

REFERENCES

1. J.P. Gollub and L.M. Sander, MRS Bull., 12, 98 (1987).
2. A. Dougherty, P.D. Kaplan, and J.P. Gollub, Phys. Rev. Lett. 58, 1652 (1987).
3. F. J. Padden, Jr., and H. D. Keith, J. Appl. Phys. 30, 1479 (1959).
4. S.W. Freiman, G.Y. Onoda Jr., A.G. Pincus in Advances in Nucleation and Crystallization in Glasses, ed. L.L. Hench and S.W.Freiman (The American Ceramic Society, Inc. 1971) pp.141-150.
5. E. Ben-Jacob, G. Deutscher, P. Garik, Nigel D. Goldenfeld, and Y. Lareah, Phys. Rev. Lett. 57, 1903 (1986).
6. K.S. Kim, and D. Turnbull, J. Appl. Phys. 44, 5237 (1973).
7. T.A. Witten, and L.M. Sander, Phys. Rev. B 27, 5686 (1983).
8. W.T. Elam et al., Phys. Rev. Lett. 54, 701 (1985).
9. L. Niemeyer, L. Pietronero, and H.J. Wiesmann, Phys. Rev. Lett. 52, 1033 (1984).
10. Gy. Radnoczi, T. Vicsek, L.M. Sander, and D. Grier, Phys. Rev. A 35, 4012 (1987).
11. D. Grier, E. Ben-Jacob, Roy Clarke, and L.M. Sander, Phys. Rev. Lett. 56, 1264 (1986).

12. Yasuji Sawada, A. Dougherty, and J.P. Gollub, Phys. Rev. Lett. 56, 1260 (1986).

13. E.P. Donovan, D.R. Brighton, D. Van Vechten, and G.K. Hubler, Mater. Res. Soc. Symp. Proc., 71, 487 (1986).

14. H.D. Keith, and F.J. Padden Jr., J. Appl. Phys. 35, 1270 (1964).

15. A. Keller in Growth and Perfection of Crystals, ed. R.H. Dovemus, B.W. Roberts, and D. Turnbull (Wiley, New York, 1958) pp. 500-532.

16. David G. Grier, David A. Kessler, and L.M. Sander, Phys. Rev. Lett. 59, 2315 (1987).

17. C.A. Carosella et al., unpublished.

18. J. Belz, E.H. Te Kaat, G. Zimmer, and H. Vogt, Nucl. Instr. and Meth. B19/20, 279 (1987).

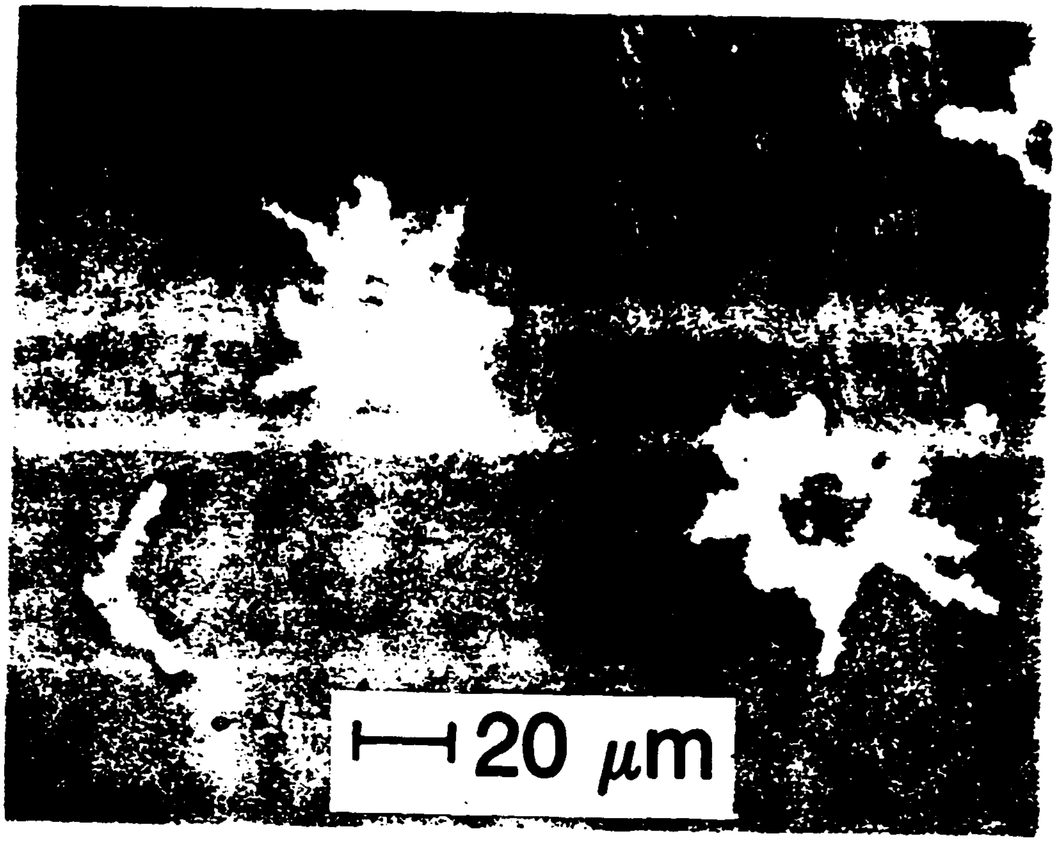
19. Benoit B. Mandelbrot, The Fractal Geometry of Nature, (W.H.Freeman and Company, San Francisco, 1982).

20. D. Bensimon, E. Domany, and A. Aharony, Phys. Rev. Lett. 51, 1394 (1983).

21. Richard F. Voss, J. Stat. Phys. 36, 861 (1984).

22. E.H. Te Kaat, and J. Belz, Mat. Res. Symp. Proc. 45, 329 (1985).

23. V.S. Kaushik, A.K. Datye, D.L. Kendall, B. Martinez-Tovar, and D.R. Myers, Appl. Phys. Lett. 52, 1782 (1988).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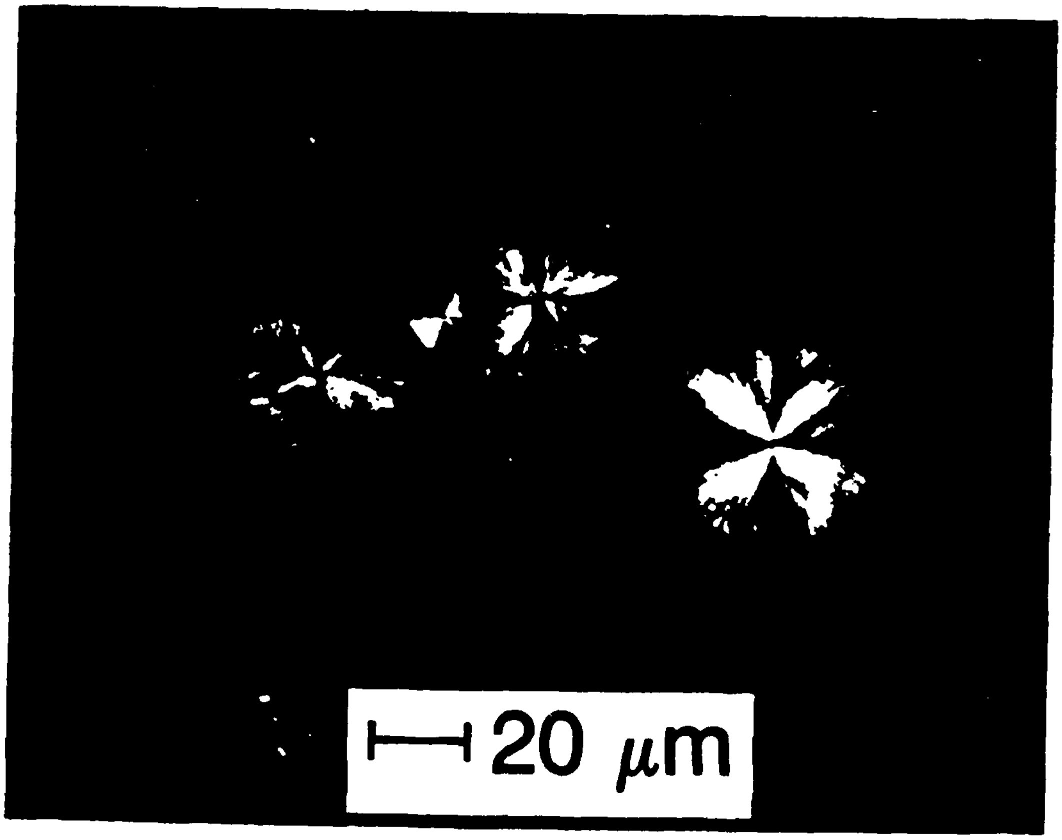
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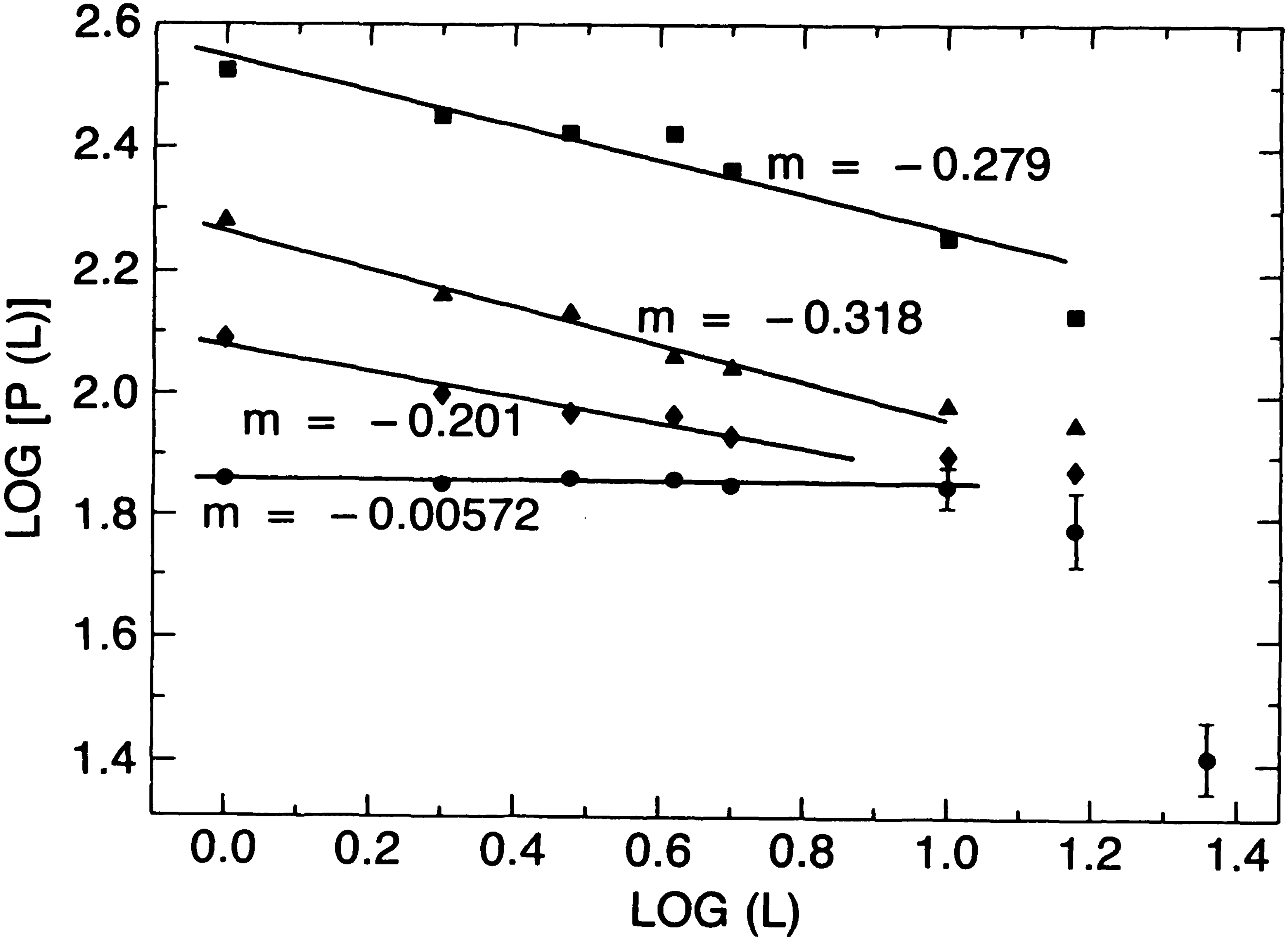
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