JOURNAL OF MATERIALS SCIENCE 28(1993) 5313–5316

# Configuration and crystallization of *a*-C:H Film on Ge and Si substrates

ZHIYUAN LIU
*Northwest University, Xian 710069, People's Republic of China*
RENJI ZHANG
*Mechanical Engineering Department, Tsinghua University, Beijing 100084, People's Republic of China*
MAILI LIU, GONGNENG YANG, QIHAI LIU, RUOBAO WANG, WANDI WANG, WANXIN JI, XIUYAN JI
*Northwest University, Xian 710069, People's Republic of China*
DA-REN HE*
*Department of Physics, Northwest University and Structure Research Laboratory, University of Science and Technology of China, Academia Sinica, Heifei 230026, People's Republic of China*

Infrared and Raman analyses on the configuration of hydrogenated amorphous carbon (*a*-C:H) thin films on monocrystalline Ge and Si substrates have been carried out. Models of the short range order and of the non-equilibrium crystallization aggregation of the films are proposed based on the analysis results and previous works by Smith [1, 2], Lu and Wang [3] and Witten and Sander [4]. The computer simulated aggregates, according to the models, are fractals with the dimension $1.81 \pm 0.06$. The films have been crystallized by laser illustration quenching. The fractal dimension of the experimentally obtained aggregates is in agreement with the simulation result.

## 1. Introduction

In our previous letter [5] a simple model was proposed to describe the connection, from microstructural aspects, between the short-range order (SRO) and the fractal dimension of the nonequilibrium crystallization aggregates (NECA) in an *a*-C:H film on a typical "soft" substrate, i.e. Se. The work may be thought of as a possible application of fractal geometry in solid state physics. The model suggests that the structural properties of an amorphous film, depending on the characteristics of its SRO, also controls, in some sense, its non-equilibrium crystallization mechanism. The fractal dimension of the NECA may then serve as a coefficient which gives some information on the microstructure of the film.

In [5] we have reported the i.r. and Raman analysis results which indicate the ratios between different $CH_n$ hybridization bonds and the ratios between the different $sp^3$-type configurations in the film. Based on the results we have also proposed a model of SRO, referring to the model suggested by F. W. Smith [1, 2]. If the film is crystallized via a phase transition far from equilibrium and then aggregated, we proposed a simple model to show the aggregates as a fractal based on the ideas of ordered-cluster shearing and deposition (CD) [3] and diffusion-limited aggregation (DLA) [4]. The fractal dimension of the aggregates is related to the configuration ratios. We have carried out a computer simulation of the model aggregation, film crystallization by ion beam bombardment, and measurement of the fractal dimension of NECA. The results are in very good agreement.

The results of our previous letter [5] have also indicated a drastic increase in the proportion of "polymer-like" SRO and a big decrease in the concentration of the "diamond-like" SRO in the *a*-C:H film on the typical soft substrate Se when compared with the proportions of SROs in the film on the standard hard substrates Si or Ge. That may reflect the tendency for the growing amorphous layer to take the structure of its substrate to reduce the interfacial stress. Since such a SRO proportions change gives rise to more "long chain-like" aggregates in our model, the fractal dimension of the NECA of *a*-C:H on Se substrate is thus expected to be much smaller than that on Si or Ge, if our model is basically correct. Therefore, it is a natural progression from [5] to report similar investigations on an *a*-C:H film on the typical "hard" substrates, Si or Ge, in this paper.

---

* To whom correspondence should be addressed at the Department of Physics, Northwest University, Xian 710069, People's Republic of China

0022–2461

## 2. Sample preparation and configuration analyses

The $a$-C:H films studied here were fabricated in a similar d.c. glow discharge system to that previously used and reported by F. W. Smith [1, 2]. Briefly, pure $C_2H_2$ at a pressure of $0.27$–$1.07 \times 10^2$ Pa was subjected to the d.c. glow discharge system ($V_d = 300$–$500$ V, $i_d = 0.5$–$2.0$ mA) and the films were deposited on monocrystalline Si or Ge substrates held at 200–300 °C. The deposition rate was 0.05–0.3 nm $S^{-1}$.

For i.r. studies $a$-C:H films were fabricated on intrinsic Ge monocrystalline substrates. Fig. 1 shows a typical i.r. transmission spectrum we have obtained. The absorption spectrum was also calculated. All the absorption bands observed and the configurations they represent are listed in Table I. The results are almost the same as those we obtained with $a$-C:H/KCl (Table I in [5]). They indicate that the percentage of $sp^1CH$, $sp^2CH_2$, and $sp^2CH$, is negligible in the studied film. The five overlapping bands between 3000 and 2800 $cm^{-1}$ which can be assigned to different $sp^3CH_n$ ($n = 1$–$3$) configurations were deconvoluted with our developed computer program, as we did before [5]. The relative ratios between various $CH_n$ hybridization bonds and $sp^3\,CH_n$ ($n = 1$–$3$) configurations were then calculated as $sp^1{:}sp^2{:}sp^3 = 0{:}0{:}1$ and $sp^3CH{:}sp^3CH_2{:}sp^3CH_3 = 0.45{:}0.33{:}0.22$. The stretching absorption of tetra-carbon ($sp^3C$–C), trigon-carbon ($sp^2C$–C) and chain-carbon ($sp^1C$–C) should appear at about 1300, 1580 and 2200 $cm^{-1}$, respectively. However, we have not observed them by i.r. As reported before (Fig. 3 in [5]), in order to certify there is some tetra-carbon and trigon-carbon in the studied film we have carried out a Raman spectroscopy study on $a$-C:H film on p-doped Si substrate ($\rho = 8$–$13\ \Omega$cm) fabricated by exactly the same d.c. glow discharge method. The spectra were in good agreement with the results of the work by Dillon *et al.* [6] and indicated that there existed some proportions of both the tetra-carbon and trigon-carbon. The proportion of chain-carbon was simultaneously certified to be negligible. It is difficult for us to obtain quantitative description of their relative ratios with only the Raman spectra. We have to make an estimation on the ratios based on the "four-components model" of the SRO in the film and the data of their relative ratios obtained by F. W. Smith. It seems reasonable to do this because our systems and the fabrication methods are almost completely the same. The four components suggested by Smith are: diamond-like ($sp^3C$–C), graphitic ($sp^2C$–C), polymeric and void. For an $a$-C:H film fabricated at 250 °C the ratios between these four components are: 0.14:0.11:0.75:0 [1]. Referring to his data, we assume that the corresponding relative ratios in the studied film are: $sp^3C$–C:$sp^2C$–C:all other configurations (all $CH_n$ hybridization bonds) = 0.14:0.11:0.75. Such an estimation will, of course, induce some inaccuracy in this investigation. However, we believe the whole description on the configuration ratios based on our i.r. analysis and this estimation is still in the reasonable range and will give rather good results.

TABLE I Predicted and observed absorption bands and the assigned configurations for $a$-C:H/Ge

| Configuration | Predicted wave number ($cm^{-1}$) | Observed wave number ($cm^{-1}$) |
|---|---|---|
| $sp^1CH$ | 3200–3305 | |
| $sp^2CH$ and $sp^2CH_2$ | 3000–3100 | |
| $sp^3CH_3$ (asym.) | 2960 | 2958 |
| $sp^3CH_2$ (asym.) | 2925 | 2925 |
| $sp^3CH$ | 2890 | 2888 |
| $sp^3CH_3$ (sym.) | 2870 | 2888 |
| $sp^3CH_2$ (sym.) | 2850 | 2850 |
| $sp^3CH_3$ and $sp^3CH_2$ (def.) | 1450–1480 | 1450 |
| $sp^3CH_3$ and $sp^3CH$ (def.) | 1370 | 1370 |

## 3. Models of short-range order and Non-equilibrium crystallization aggregation

In this section we give a brief statement of our models of SRO and NECA, which are basically the same as stated before in [5].

We will organize the results of our i.r. analysis and of the estimation based on our Raman analysis and the data of F. W. Smith together to give a whole description on the configurations in the studied $a$-C:H film, as stated in Table II. In Table II we divide the observed configurations in our film into four groups according to their characteristics and functions. They are: mono-stretching direction configuration (MSDC), bi-stretching direction configuration (BSDC), tri-stretching direction configuration (TSDC), and tetra-stretching direction configuration (TTSDC). TTSDC ($sp^3C$–C) is the only "real" dia-

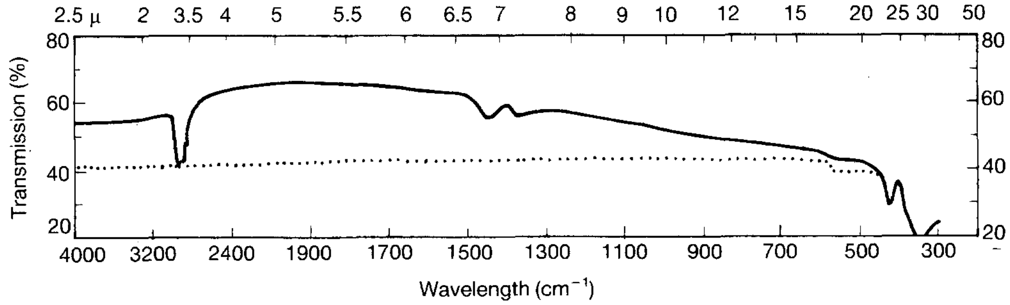
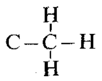
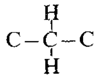
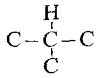
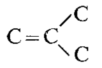
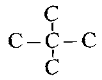


*Figure 1* A typical transmission spectrum of $a$-C:H/Ge (solid line) and of Ge (dashed line).

TABLE II Configuration groups in $a$-C:H on Si or Ge

| Name | Symbolic expression | Approximate percentage | Number of stretching directions | Configuration expression |
|---|---|---|---|---|
| MSDC | $sp^3CH_3$ | 16.5 | 1 |  $\mathrm{C{-}\overset{H}{\underset{H}{C}}{-}H}$ |
| BSDC | $sp^3CH_2$ | 24.7 | 2 |  $\mathrm{C{-}\overset{H}{\underset{H}{C}}{-}C}$ |
| TSDC | $sp^3CH$ | 33.8 | 3 |  $\mathrm{C{-}\overset{H}{\underset{C}{C}}{-}C}$ |
|  | $sp^2C{-}C$ | 11 | 3 |  $\mathrm{C{=}C\genfrac{}{}{0pt}{}{\diagup C}{\diagdown C}}$ |
| TTSDC | $sp^3C{-}C$ | 14 | 4 |  $\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}C}$ |

mond-like configuration, which forms only a small percentage of the film. To answer the question why a film with such a small proportion of TTSDC can show significant hardness (as we measured it, the Knoop hardness of the film is over $1.96 \times 10^2\ \mathrm{N\,mm^{-2}}$), we propose that a SRO can be organized where TTSDC serves to bind TSDC (mainly is $sp^3CH$) which lost one stretching direction altogether. The basic structure of the SRO should still be "diamond-like". Hydrogen atoms in $sp^3CH$ can be thought of as terminating the dangling bonds in this diamond-like SRO region. The other SRO suggested is the "polymer-like" one organized bv BSDC, as suggested by F. W. Smith [1, 2]. MSDC can only terminate dangling bonds in the two kinds of SRO as the function of a hydrogen atom. We can thus calculate the relative bond ratio between these two kinds of SRO in our film as: diamond-like:polymer-like = 2.4. It is much larger than the ratio 0.66 in the film on Se substrate [4].

Recent studies have revealed that the initial growth mechanism with the lowest crystallization energy of amorphous solids is that in which the original SRO forms some ordered clusters. Then the growth of crystals and/or embryos is composed of two kinds of process: single atoms jumping or diffusing (AJ) from the amorphous matrix to the crystal front, and ordered clusters shearing and depositing onto the growing crystal (CD) [3]. In a rapid crystallization process far from equilibrium we propose that the randomly distributed ordered clusters are growing and stretching in certain directions according to their order structure (AJ). They connect to one another with some shearing when their boundaries encounter (CD). Such a process can be described by a "multicentre DLA model". We suppose that a number of ordered clusters are randomly distributed and then other clusters randomly move on the surface until they encounter and then bond to one of the centre clusters. The aggregates formed by this model should be a fractal with good scaling-invariance properties [4].

Based on our SRO model there are only two kinds of ordered clusters in the fast crystallization-aggregation. They are tribranching clusters (TB) formed by TTSDC and TSDC, and the dibranching clusters formed by BSDC (DB). If we assume that every cluster is of average size, we can estimate the ratio between TB and DB as also being 2.4.

## 4. Computer simulation and experiment verification

Computer simulation has been performed based on the above model of NECA with the ratio $n_2$ (TB): $n_3$ (DB) = 2.4:1.0 on a triangle lattice. The simulated figures show much more bifurcation and much fewer "long chains" when compared with the corresponding figure (Fig. 5) in [5]. The fractal dimensions of the figures were calculated by the Sandbox method [7]. Good scaling properties were found, as shown in Fig. 2. If we define the "density of the figure" as $k$

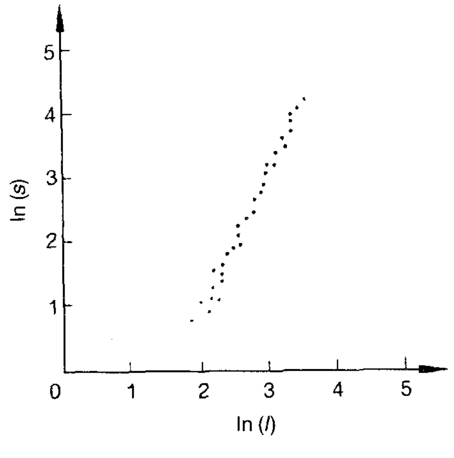


*Figure 2* The scaling behaviour of a computer simulated figure of NECA of an $a$-C: H film on Si or Ge substrates. The "density of figure" is $k = 0.107$. $n_2$(TB):$n_3$(DB) = 2.4. $l$ is the length of the taken box in the Sandbox method. $s(l)$ is the number of clusters inside box when the centre of the box coincides with the centre of mass of the figure in the box. The fractal dimension, i.e. the slope obtained by least square fitting of the $\ln(s)$–$\ln(l)$ data is $1.80 \pm 0.04$.

$= (n_2 + n_3)/n_1^2$, where $n_1$ is the total number of lattice points, the fractal dimension is always in the region of $1.81 \pm 0.06$ when $k$ changes from 0.07 to 0.22 and when the ratio $n_2:n_3$ takes the constant value 2.4. This value of fractal dimension is obviously larger than that of 1.37 for aggregates of $a$-C:H on Se substrate [5].

The studied $a$-C:H/Si samples have been crystallized by laser illustration quenching. The output beam of a continuous $CO_2$ laser was directed onto the surface of the sample for a very short time (1–2 s). The power density in the illustrated region was over $2000\ W\ cm^{-2}$. The $a$-C:H film was very quickly heated by the absorption by the substrate (the resistivity of the Si substrate was 8–13 Ω cm). and then quickly cooled by an electric fan. After quenching the samples were observed by SEM at different magnifications. The aggregates are fractals with much more bifurcations and much fewer long chains, as predicted by the computer simulation. Fig. 3(a) shows one of the SEM plates. The photographs were then digitized and the fractal dimensions of the aggregates were calculated using a program of the Sandbox method. The fractal dimension of Fig. 3(a) was calculated as $1.71 \pm 0.05$ with very good scaling behavior, as shown in Fig. 3(b). The values of the fractal dimension calculated with other SEM images are about same. The results of the experiment and the computer simulation are in agreement. The deviation is little larger than that in the case of $a$-C:H on the soft substrate [5]. That may be due to the inaccurate values of the concentration of $sp^3$C–C and $sp^2$C–C.

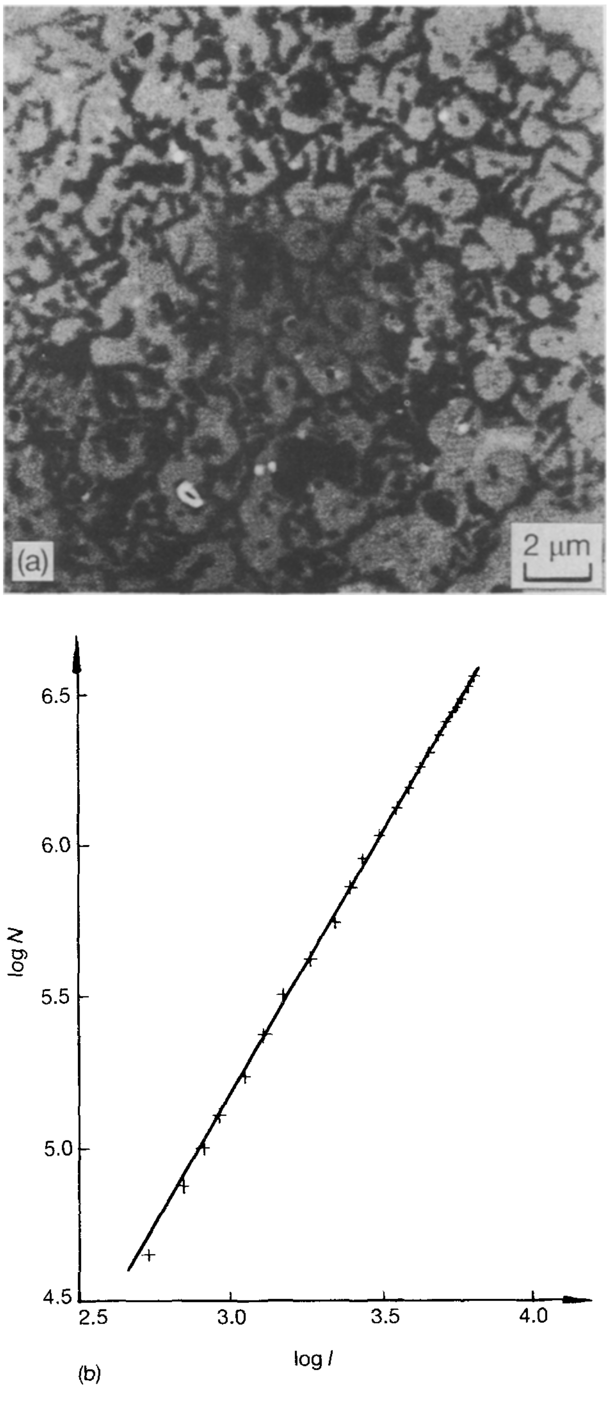


*Figure 3* (a) A SEM plate of the aggregate of $a$-C:H/Si after laser illustration quenching. (b) The scaling behaviour of Fig. 3(a). The meaning of $N$ and $l$ are the same as $s$ and $l$ in Fig.2(b). The slope of the solid line, which is the least square fitting of the data, i.e. the fractal dimension of the aggregate, is $1.71 \pm 0.05$.

## 5. Conclusion

This paper gives another sample investigation on the microstructure and the non-equilibrium crystallization aggregation of the $a$-C:H films. It may serve as the second proof for our model of NECA. We believe the idea of the model can be used in NECA of other amorphous materials and hope our results can stimulate more interest in possible applications of fractal geometry in solid state physics.

## Acknowledgements

The authors thank Prof. F. W. Smith and Prof. M. P. Sarachik of the City College of New York for their help with many aspects of our research. Helpful discussions with Dr B. Dischler of the Frauhofer-Institute and Dr K. Lu and Prof. J. T. Wang of the Institute of Metal Research in Shenyang and their reprints are also gratefully acknowledged. One of us (He) would like to express his thanks also to Prof. Dr. W. Martienssen and all his colleagues in his group at the Physics Institute of the University Frankfurt for the help and hospitality while this paper was being written. This work was supported by the Structure Research Laboratory, University of Science & Technology of China.

## References

1. F. W. SMITH, in "Preparation and characterization of amorphous carbon films", edited by J. J. Pouch and S. A. Alterorits (Trans Technical Publications, Switzerland, 1990).
2. *Idem. J., Appl. phys.* **55** (1984) 764.
3. K. LU and J. T.WANG, *J. Cryst. Growth* **94** (1989) 448.
4. T. A.WITTEN and L. M.SANDER, *Phys. Rev. Lett.* **47** (1981) 1400.
5. D.-R. HE, X. Y. JI, R. B. WANG, Q. H. LIU, W. D. WANG, M. L. LIU, W. Z. CHEN, Z. Y. LIU, W. X. JI and R. J. ZHANG, *J. Mater. Sci. Lett.* **9** (1990) 1371.
6. R. O. DILLON, J. A. WOOLLAM and V. KATKANAUT, *Phys. Rev. B* **29** (1984) 3482.
7. S. R. FORREST and T. A. WITTEN, *J. Phys. A* **12** (1979) L109.

*Received 27 April 1992*
*and accepted 24 February 1993*