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# Formation of ordered structures in the thin-film amorphous carbon/silicate glass system

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solution would be helpful in considering this question further.

In conclusion, it seems clear from the present study that TAA<sup>+</sup> ions form a blocking layer at negative potentials on a polarizable electrode when they are adsorbed from aprotic solvents. The thickness of this layer increases with the length of the alkyl chain but is not simply related to the crystallographic radius of the TAA<sup>+</sup> ion as is seen from differential capacity data. Electron transfer occurs by tunneling through the resulting organic layer, more probably by elastic transitions,<sup>42</sup> to the redox system in solution. Much more needs to be learned about this process, and further experiments should be carried out. These should involve a series of structurally similar redox systems of relatively simple nature but with a wide range of standard potentials. The role of the solvent also needs to be further elucidated as far as the tunneling process is concerned.

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**Registry No.** Hg, 7439-97-6; Nm, 603-71-4; TEAP, 2567-83-1; TPAP, 15780-02-6; TBAP, 1923-70-2; THxAP, 4656-81-9; TOAP, 25423-85-2; PC, 108-32-7; TEA<sup>+</sup>, 66-40-0; TPA<sup>+</sup>, 13010-31-6; TBA<sup>+</sup>, 10549-76-5; THxA<sup>+</sup>, 20256-54-6; TOA<sup>+</sup>, 19524-73-3; AN, 75-05-8; DMF, 68-12-2; DMSO, 67-68-5; HMPA, 680-31-9; NP, 79-46-9.

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## Formation of Ordered Structures in the Thin-Film Amorphous Carbon/Silicate Glass System

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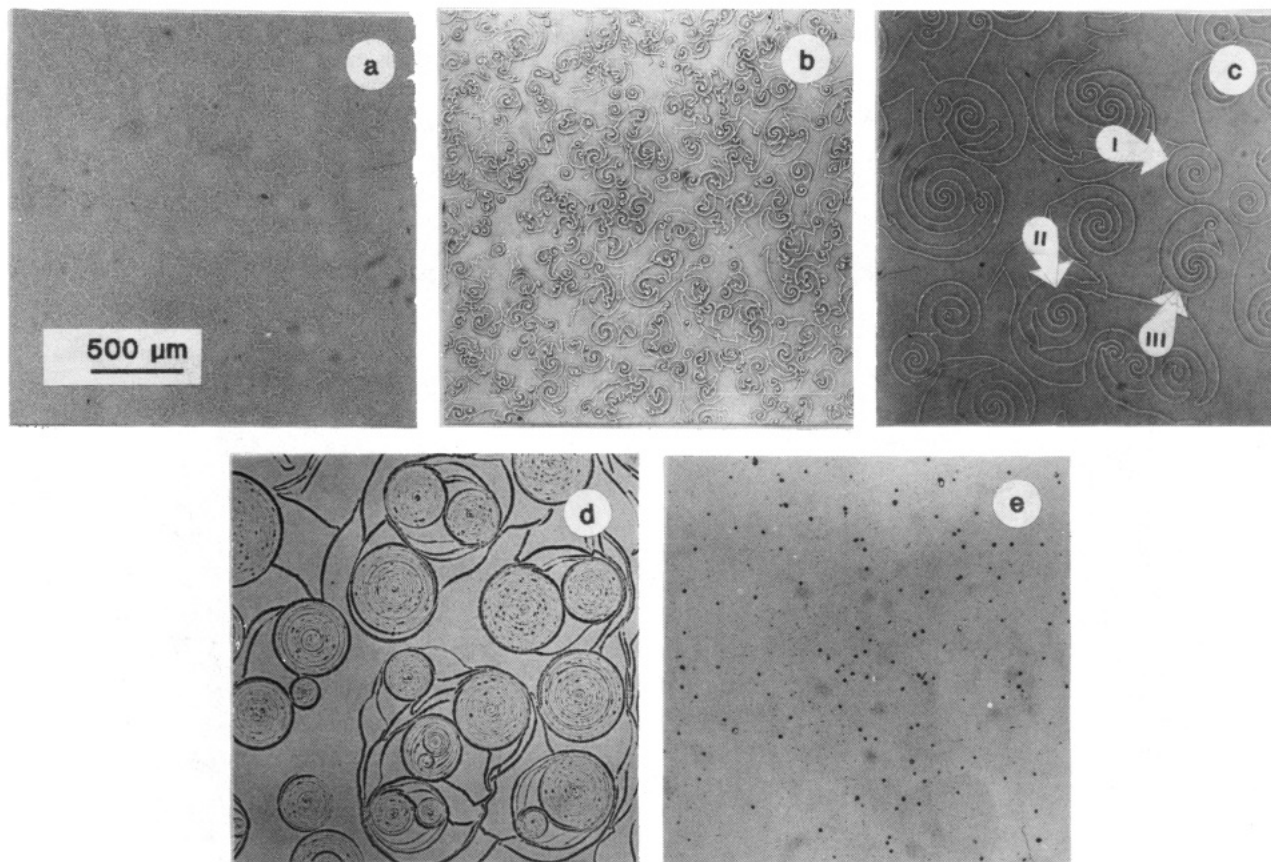
A system thin film of amorphous carbon arc evaporated in vacuum on glass substrate is studied. By applying suitable decoration procedures, microscopic defects having spirallike symmetry are visualized in the glass substrate. It is established that the value of the background pressure in the vacuum chamber, the film thickness, and the chemical composition of the substrate surface are basic factors determining the spiral formation. The peculiarities in the spiral morphology give the reason the observed structures to be regarded as a result of a self-organization phenomenon.

## Introduction

The interest toward ordered structures formed as a result of self-organization phenomena in various physical, chemical, and biological systems has considerably increased following the discovery of organizing centers in the Belousov-Zhabotinski (BZ) reaction.<sup>1</sup> Depending on the experimental conditions, different

types of autowave structures can be initiated such as "target" patterns, "fronts", and spiral waves resulting from "front" breaking,<sup>2</sup> spirals with a topological charge greater than unity,<sup>3,4</sup> and the quasi-stochastic regime.<sup>5,6</sup> In fact such structures have already been observed but they have been regarded as Liesegang rings.<sup>7-11</sup> Recently, a complete set of these self-organization phenomena has been obtained during electrodeposition of Ag-Sb metal alloys.<sup>12</sup>

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**Figure 1.** Optical transmission micrographs of decorated defects in Na-Ca-silicate glass after deposition of thin film of amorphous carbon with different thicknesses: 10 (a), 30 (b), 40 (c), 50 (d), and 60 nm (e). The arrows on (c) show one (I), two (II), and three (III) armed spiral structures. Residual gas pressure  $4 \times 10^{-4}$  Pa.

During transmission electron microscopy (TEM) studies of Na-Ca-silicate glass plates by means of the shadowing technique, we have observed ordered defects both in the carbon film and in the glass samples after the replica separation from the surface studied. It was established that such ordered structures are not present in the initial glass substrates. Therefore, they are introduced during the vapor deposition of the amorphous carbon on the glass substrate. It is clear that for TEM studies these artificial defects are undesirable and they must be avoided. On the other hand, it is very fascinating that ordered patterns are created in a completely disordered solid-state system.

The present paper aims to reveal the nature of ordered pattern formation in the solid-state system of amorphous carbon on glass substrate.

### Experimental Section

The samples were prepared in a standard vacuum unit HV B-30.1 (VEB Hochvacuum Dresden, Germany) by arc evaporation of spectrally pure graphite on precleaned Na-Ca-silicate glass plates.<sup>13</sup> The precleaning procedure comprises 8 min of mechanical polishing by means of  $\text{CeO}_2$  and 10 min of processing in a solution of 10 g/L  $\text{K}_2\text{Cr}_2\text{O}_7$  in  $\text{H}_2\text{SO}_4$  at 90 °C. Then, the drying of the glass plates was preceded by a treatment in pure ethyl alcohol. The starting substrate temperature was ambient, e.g., in the range from 15 to 20 °C. However, during the arc deposition of carbon it slowly increases, reaching a maximal value of 70–80 °C at the end of the evaporation process. The measurement of the substrate temperature was carried out by means of a differential thermocouple. The latter was screened from the influence of the considerable mass-energy flow, typical for the vacuum deposition technique used. At vacuum better than  $6 \times 10^{-4}$  Pa and a constant distance between the evaporation source and the substrate of 12 cm, the mean deposition rate of carbon was in the order of 5 nm/s. Thus, film thickness ranging between 3 and 60 nm was obtained by varying the time of deposition only. Some experiments were performed under different background pressures in the range from

27 to  $6 \times 10^{-4}$  Pa using as a residual gas dry air, dry pure nitrogen, or dry pure argon. Comparative studies were also performed on substrates of fused quartz glass plates as well as Na-Ca-silicate glass deliberately modified either by ion bombardment or by ion exchange in molten  $\text{KNO}_3$ . In the last case the substrates were processed for 8 h in the  $\text{KNO}_3$  melt at 350 °C, followed by the standard precleaning procedure.<sup>13</sup> For the purposes of ion bombardment experiments the evaporation chamber was first evacuated to vacuum better than  $4 \times 10^{-4}$  Pa. Then a pure dry gas, nitrogen or argon, was leaked through a needle float to a background pressure of about 100 Pa. A glow discharge arrangement with a circular segment shape, original for the vacuum unit used, was disposed at 10 cm from the glass substrates. The ion bombardment procedure was carried out under moderate conditions, usually  $100 \mu\text{A}/\text{cm}^2$  at 200 V and a processing time from 1 to 30 min. Further, the gas inlet was shut off and the deposition of carbon film was performed after recovering the initial high-vacuum conditions.

By means of transmission electron diffraction it was established that in the whole range of preparation conditions the structure of carbon films remains always amorphous.

The specimens thus obtained were treated for 1–5 min with diluted HF acid at 20 °C. Then the carbon film was separated from the substrate in distilled water. Thus, different kinds of defects are visualized both in the self-supporting carbon film and on the glass surface. The same decoration effect was obtained also by sample treatment at 88% relative humidity and 60 °C for 72 h. In the present paper only the defects revealed in the glass plates were inspected under an optical microscope "Amplival" (Carl Zeiss, Jena, Germany).

### Results and Discussion

The influence of the amorphous carbon film thickness on the spiral formation is demonstrated in Figure 1. It is clearly seen that, depending on the thickness of the deposited carbon thin film, several kinds of defects are observed. However, the formation

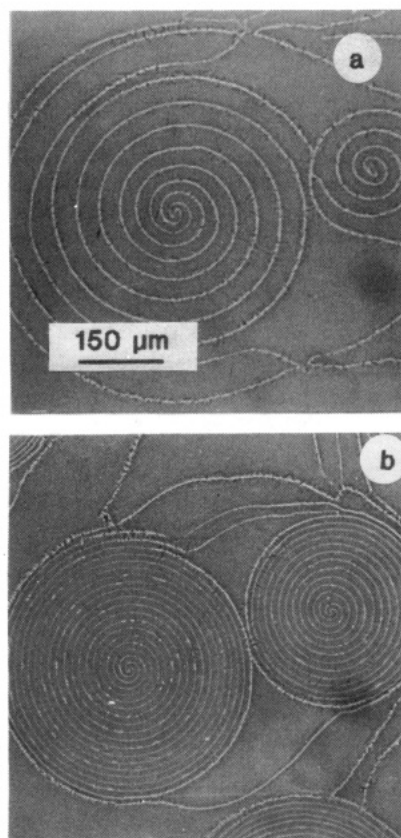


**Figure 2.** Optical transmission micrographs of decorated defects in Na-Ca-silicate glass after deposition of 50-nm-thick film of amorphous carbon at different nitrogen gas background pressures: 27 (a), 5.3 (b), and  $6 \times 10^{-4}$  Pa (c).

of spiral structures is favored for film thicknesses from 30 up to 50 nm (Figure 1b-d). Simultaneously, the increase of the film thickness leads to a reduction of the spiral pattern spacing. Above 50 nm only a quasi-stochastic regime of defect formation<sup>5,6</sup> is observed (Figure 1e). An analogous regularity has been found when studying the influence of different layer depths on an oscillatory BZ reagent.<sup>14</sup>

The role of the background pressure in the vacuum chamber on the defects studied is illustrated in Figure 2 for the film thickness of the deposited 50-nm amorphous carbon. Obviously, the formation of ordered structures is favored at pressure values lower than 5.3 Pa (Figure 2b). Further decrease of the background pressure leads to the formation of comparatively perfect spirals (Figure 2c). At vacuum higher than  $4 \times 10^{-4}$  Pa a quasi-stochastic regime as shown on Figure 1e is achieved. It was found that the results obtained are not changed when, instead of nitrogen, dry pure air or argon was used as background gas.

The chemical composition of the substrate also influences substantially the formation of ordered structures (Figure 3). On



**Figure 3.** Optical transmission micrographs of spirals decorated in Na-Ca-silicate glass (a) and after modifying the glass surface by exchange of Na by K ions (b). Carbon film thickness 45 nm.

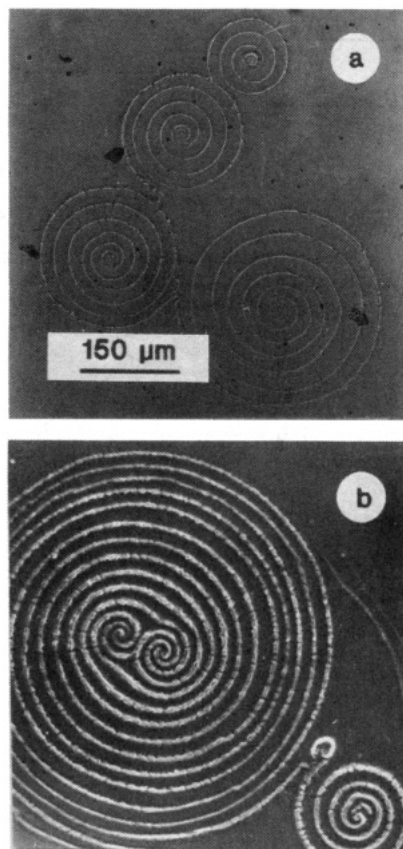
the initial Na-Ca-silicate glass the spacing of spiral patterns is greater (Figure 3a) than the spacing on the substrate subjected to an exchange of Na with K ions (Figure 3b). It should be noted that the ion exchange procedure itself could introduce additional microdefects which might affect the spiral formation. Following this assumption an additional set of experiments was carried out using the ion bombardment technique. Under moderate conditions this procedure also creates active centers without incorporation of new chemical species in the glass surface. It was established that short-time ion bombardment does not change either the concentration or the parameters of the spiral structures on Na-Ca-silicate glass. However, above 15 min of ion bombardment the spiral patterns disappear completely. These results are not affected by the type of the background gas used, nitrogen or argon.

On the other hand, the evaporation of amorphous carbon on fused quartz glass plates does not initiate the formation of spirals or other kind of defects already revealed on the initial glass substrate. Since chemically the fused quartz is pure  $\text{SiO}_2$ , it could be concluded that the alkali-metal ions in the glass surface region play a substantial role in spiral formation process.

As seen from the figures presented above, the spirals are the major defects in the system amorphous carbon/silicate glass. It should be emphasized that in all cases this defect pattern can be approximated to the Archimed spiral since they have equal spacing between sequential turns. On the other hand, there is not a favorable direction of spiral rotation—clockwise or counter-clockwise. In both cases one-, two-, and three-armed spirals are visualized (Figure 1c; I, II, III). Moreover, they interact in a manner which is typical for autowave processes, leading to annihilation (Figure 4a) or formation of a common organizing center (Figure 4b).

It should be noted that in some cases besides the spirals, the decoration procedure reveals a new phase with crystallike morphology. As seen from the micrographs on Figures 3a and 4a, this phase is localized only within the region of spiral formation. Similar results have been obtained during an investigation of Liesegang's periodic structures in solid solutions.<sup>15</sup>





**Figure 4.** Optical transmission micrographs of annihilated spirals having opposite rotation directions (a) and common organizing center (b). Carbon film thickness is the same as in Figure 3.

At present the complexity of the phenomenon studied makes difficult an unambiguous explanation of the general mechanism involved. Nevertheless, different processes, as for example specific carbon thin film growth phenomena, cracks generation resulting from internal stresses, or thermally induced crystallization, could be supposed. Further experiments which are in progress will help for a better understanding of the intimate mechanism of spiral formation.

## Conclusion

Summarizing the results obtained, it should be noted that the present study gives the first experimental evidence of spirallike structure formation in the system: thin films of amorphous carbon/silicate glass. The appearance of such structures as a sequence of mass-energy flow through the system, the presence of spirals with topological charge equal or greater than unity, and the annihilation of two wave fronts are essential characteristics of the investigated process. It seems that this is not an unique case taking into account the results published on other solid-state thin-film systems.<sup>16-18</sup>

On this basis the formation of spiral structures in the system reported could be attributed to the more general self-organization phenomena.

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**Registry No.** Carbon, 7440-44-0.

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## Studies of the Changes Occurring on Reduction and Reoxidation of Cu-Y Zeolites

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The possibility that Cu-Y zeolites are dealuminated during reduction with H<sub>2</sub> (at 473 K) or with CO (at 773 K) was investigated by XRD and by <sup>29</sup>Si and <sup>27</sup>Al MAS NMR. H<sub>2</sub>/O<sub>2</sub> and CO/O<sub>2</sub> cycles were also examined. Stoichiometric determinations of the oxidation and reduction steps were determined separately to compare the chemistry occurring using CO or H<sub>2</sub> as the reducing agents. Although some dealumination was detected under certain conditions, the amount was much less than that required to charge-balance the lattice on the conversion of Cu<sup>2+</sup> to Cu<sup>+</sup>. Evidence is presented that extralattice oxygen is introduced during the preparation steps.

## Introduction

When zeolites are loaded with altrivalent base-exchange cations, e.g., Fe<sup>2+</sup> or Cu<sup>2+</sup>, they become oxygen carriers.<sup>1-3</sup> For example

Fe<sup>2+</sup>-Y could be oxidized with O<sub>2</sub> forming Fe<sup>3+</sup>-Y with the concomitant addition of one oxygen atom for every two Fe<sup>2+</sup> oxidized.<sup>1,2</sup> The Fe<sup>3+</sup>-Y could in turn be reduced back to Fe<sup>2+</sup> with the formation of a stoichiometric amount of H<sub>2</sub>O. This reduction process could be carried out at temperatures as high as 1000 K without reducing the catalyst further to Fe<sup>0</sup>. Thus a stable redox system was formed. This work was extended in our laboratory<sup>3</sup> to show that NO and/or N<sub>2</sub>O could be substituted for O<sub>2</sub> as the oxidizing agent and that CO could be substituted

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