Communications to the Editor

Spontaneous Formation of Periodically Patterned Deposits by Chemical Vapor Deposition

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Patterns of colloidal origin that are formed in ionic precipitation−diffusion systems and are known as Liesegang Rings (LR)[1] have fascinated researchers since the beginning of the century and have been the subject of numerous theoretical, numerical, and experimental studies.[1−4] The terms recurrent, rhythmic, or periodic precipitation are often used to describe the temporal pattern evolution in such systems. Pattern formation in the vapor phase reaction of NH_3 and HCl has also been reported since 1930.[5] It has been suggested that any reaction giving an insoluble product is capable of LR pattern formation.[2,3] However, the potential of such self-organized deposition for the fabrication of materials (other than NH_4Cl) from vapor precursors has not been demonstrated. Moreover, reproducible LR patterns are usually characterized by uneven spacing (Matalon−Packter law)[6,7] and band thickness, although nearly periodic patterns have been reported as well. Here we propose, for the first time, a connection of LR phenomena, with the spontaneous (i.e., involving no external concentration, temperature, or other parameter forcing) formation of micrometer size periodic stripes of nanocrystalline titania deposited in mesoporous glass by counter diffusion chemical vapor deposition (CVD) using titanium chloride and water.[8]

TiO_2 is a well-known wide band gap semiconductor and photocatalyst and its incorporation in mesoporous silica has been reported in the context of numerous applications.[8,9] The use of $TiCl_4$ for CVD and vapor phase particle formation has been widely employed.[8,10] The deposition of TiO_2 in porous silica from titanium chloride is proposed to proceed with an agglomeration mechanism that involves intermediate $Ti(OH)_{(4-x)}Cl_x$ ($x = 1-3$) volatile species.[11] Moreover, the gas-phase reaction of $TiCl_4$ and H_2O is believed to proceed by the fast formation of $Ti(OH)_2Cl_2$ species followed by slow further hydrolysis leading to TiO_2 and HCl.[12] Thus TiO_2 formation, through both gas-phase and surface pathways, can be qualitatively described by the reaction scheme characteristic of recurrent precipitation systems,[1−3] i.e.:

$$\mathrm{A(vapor) + B(vapor) \rightarrow C(vapor) \rightarrow D(solid)}$$

where A is the metal chloride, B is the water, and C are metal oxy- or hydroxy-chloride volatile species. The produced HCl is neglected in this representation since it appears not to participate in the deposition at the conditions used.[11,12] When the concentration of C exceeds a certain level the deposit metal oxide, D, nucleates and grows with further consumption of C and/or A and B. Simulations based on this scheme with various nucleation and growth rate expressions and transport mechanisms result, under certain conditions, in LR patterns.[2,3,5] Periodic deposit formation can originate from two reported schemes. One possibility[13] follows ideas for stationary periodic pattern originally proposed by Turing.[14] In this mechanism, a spatially uniform solution of the diffusion-reaction equations becomes unstable to spatial perturbations giving rise to stationary patterns by an activator−inhibitor self-organization mechanism due to competition of diffusion and autocatalytic (activator−inhibitor type) chemistry. If the product of the reaction serves as a precursor of nucleation and growth, it can imprint its periodic pattern into a solid deposit.[13] A major challenge in experimental manifestation of such diffusion−reaction instabilities is that the ratio of diffusivities of the inhibitor and activator is usually large (e.g., an order of magnitude difference). Such difference cannot be achieved easily in gas- and liquid-phase systems with species of similar molecular weights. However, nanoporous substrates like Vycor are ideal for creating such large differences. A second mechanism of periodic pattern formation, of a mathematically similar instability to Turing, results from the competition of microphase separation driven by attractive intermolecular forces and a simple chemical reaction.[15,16] Such instabilities have been examined in block copolymers and adsorbates on surfaces undergoing a chemical reaction. A similar mechanism was recently employed in modeling LR formation.[7] Although the study in ref 7 emphasized conditions leading to the Matalon−Packter law it is also stated that nearly periodic patterns could form at the initial stages of pattern evolution under certain conditions.[7] It should also be noted that the referenced modeling studies do not account for the effect of pore blockage on the transport of the reactants and intermediate species. This may be important here since as revealed from Transmission Electron Microscopy the deposit fills the substrate pores near the percolation threshold (see discussion below). At this point we are unable to quantitatively simulate TiO_2 formation at the experimental conditions described bellow since a detailed mechanism with associated parameters is not available.

A schematic of the deposition geometry that resulted in the formation of periodic patterns is shown in Figure 1a. $TiCl_4$ and H_2O are carried by N_2 carrier gas streams passed through the corresponding saturators and introduced from opposite sides of a porous glass substrate tube. The porous glass substrate is Vycor

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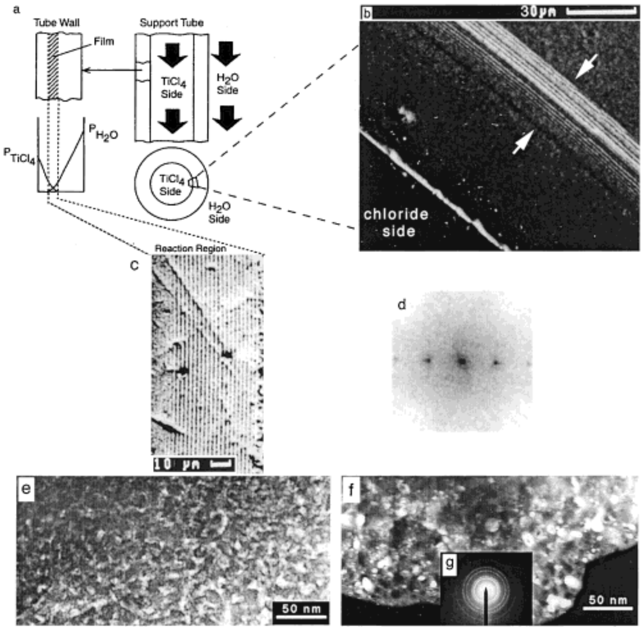

Figure 1. Deposition of titania with periodic deposit density variations: (a) schematic of the deposition geometry; (b) BSEM of a cross section after deposition (30 min, 600 °C, using 10% water and 20% chloride feeds); (c) BSEM of a cross section (30 min, 450 °C, 10% water and 20% chloride feeds); (d) optical diffractogram, from Figure 1c; (e) TEM of the pores of the substrate without deposit present; (f) dark field electron micrograph of nanocrystalline deposit in the pores of the substrate; (g) selected area diffraction pattern from the region shown in Figure 1f.

glass. The $N_2/TiCl_4$ stream is flown in the interior of the tube (chloride side) whereas the N_2/H_2O stream is introduced in the annulus (water side). Due to the small pore size (average pore diameter ~4.7 nm) of the substrate, transport takes place without any convective contribution. The two reactants diffuse and react to give TiO_2 according to the overall reaction:

$$\mathrm{TiCl_4(vapor) + 2H_2O(vapor) \rightarrow TiO_2(solid) + 4HCl(vapor)}$$

The reaction zone can be controlled from deep inside to close to the surface of the support by adjusting the concentrations of $TiCl_4$ and H_2O in the feed streams.[8]

As stated above this reaction involves intermediate volatile species and mechanistically belongs to the reactions producing LR patterns.

Results from the examination of the deposit by Back-Scattered Electron Microscopy (BSEM), Transmission Electron Microscopy (TEM), and Electron Diffraction (ED) show clearly that a nanocrystalline titania deposit with micrometer size periodic density variations has been formed (Figure 1). The BSEM images were collected after cutting the substrate, polishing, and coating with carbon. The TEM images were recorded using a Philips 430 EM operated at 100kV. Microtomy or mechanical thinning and ion milling prepared samples were used.

The Vycor glass substrate has uniform microstructure at length scales larger than the characteristic pore diameter (~5 nm)[17] and, therefore, the observed micrometer size deposit patterns cannot be attributed to a patterned substrate. Their formation is driven as in LR patterns from the interplay of reaction and transport. Figure 1b shows a BSEM of a cross section after deposition for 30 min at 600 °C using 10% water and 20% chloride feeds. The nearly periodic alternation of bright and dark bands, in the area between the arrows, originates from atomic number contrast due to deposit density variations. Under different deposition conditions (30 min, 450 °C, 10% water and 20% chloride feeds), Figure 1c shows that the distance between the stripes is increased to 2.5 μm as opposed to the approximate 2 μm spacing in Figure 1b and that the deposit pattern periodicity extends over a larger distance. Figure 1d shows the optical diffractogram from Figure 1c. The first- and second-order sharp reflections confirm the periodic density variations of the deposit. Further experimentation shows that deposition using the same concentrations at 200 °C does not result in a banded deposit. That and the optimal pattern periodicity for deposition at 450 °C as opposed to the less ordered deposit formed at 600 °C emphasize the importance of the coupling of the nucleation and deposition kinetics with the transport of reactants and intermediate species as is typical in LR phenomena. Characteristic of other reported LR patterns is also the time evolution of the deposits, i.e., the patterns are not formed simultaneously but rather evolve in time. Figure 1e is a TEM of porous glass showing the pore structure of the substrate without deposit present while the dark field electron micrograph of Figure 1f is showing nanocrystalline deposit filling the pores of the substrate to the percolation threshold. Finally, the selected area diffraction pattern of Figure 1g taken from the region shown in Figure 1f confirms the presence of nanocrystalline TiO_2 (predominantly anatase with a smaller amount of rutile). We have found that the crystal structure can be varied by changes in the deposition and/or annealing temperature.

The reported results establish that LR phenomena occur in a well-known class of technologically important reactions (CVD of metal oxides). The simplicity and generality of the deposition scheme suggest that similar deposition leading to microscopic periodic pattern formation in the interior of porous substrates may occur in other classes of deposition reactions as well. Pattern formation relying simply on self-regulation during diffusion, reaction, and deposition in porous substrates, if combined with the recent progress in the fabrication of ordered porous media,[18] may result in an efficient, single-step technique in the quest for multiscale organization.

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