Pattern Formation of Zinc Nanoparticles in Silica Film by Electrodeposition

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Zinc nanoparticles were grown within gel-derived silica films by applying a direct current voltage. Pattern formation of metallic Zn was studied as a function of applied voltage and metal—silica ratio. Average particle size varied from 5.2 to 20.2 nm by changing the applied voltage and silica concentration. It was found that the transition from fractal to dendritic morphology was possible due to crystalline anisotropy. From high-resolution transmission electron microscopy images and X-ray diffraction pattern a possible model is proposed to explain this observation.

Introduction

Growth of metal nanoparticles by electrodeposition has received considerable attention in recent years because of their fractal geometry and dendritic growth.¹⁻⁴ The latter has been studied extensively as a model for understanding diffusionlimited growth phenomena.⁵ In most of these electrodeposition experiments an aqueous solution of electrolyte with a ringlike anode and a sharp-tip cathode was used. The interesting aspect of these experiments is the reason behind some patterns to be dendritic while the others are fractal. In general, the transition from fractal to dendritic structure is possible when anisotropy dominates over random noise in the growth process.² In electrochemical deposition, this type of transition is observed when growth speed is increased.^{2,3} In the present work, we have grown both fractal and dendritic structures of zinc nanoparticles inside a silica film by the electrochemical deposition process. We have also studied the crossover from fractal to dendritic growth in two dimensions on the microscopic scale. Dendritic to stringy transition has also been observed at very high growth speed. Detailed microstructural analyses through high-resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD) patterns of these films show that the crystalline anisotropy in the nanometer range growth is the reason behind phase transition in the micrometer range pattern formation. This mechanism has also been established through a crystallographic growth model. From XRD pattern and HRTEM images a model is proposed to show how anisotropy in nanometer scale generates this transition in the micrometer scale. The details are reported in this paper.

Experimental Section

The target composition chosen for the gel was $xZn(NO_3)_2$, (100 - $x)SiO_2$ (where x was varied from 20 to 50). The solgel films with different ratios of $Zn(NO_3)_2$ and SiO_2 prepared are summarized in Table 1. The precursors used were $Zn(NO_3)_2$ and $Si(OC_2H_5)_4$. Zinc nitrate salt was dissolved in distilled water and ethyl alcohol solution, which was stirred by a magnetic stirrer. A few drops of dilute HNO₃ was mixed to keep the pH level ~4. Weighed amount of tetraethyl orthosilicate (TEOS)

TABLE 1: Sol–Gel Films with Different Ratios of $Zn(NO_3)_2$ and SiO_2

specimen no.	composition
1	20Zn(NO ₃) ₂ , 80SiO ₂
2	30Zn(NO ₃) ₂ , 70SiO ₂
3	$40Zn(NO_3)_2, 60SiO_2$
4	50Zn(NO ₃) ₂ , 50SiO ₂

was mixed dropwise when the solution was stirred. The volume ratio of water, alcohol, and TEOS was kept at 5:5:1. This mixture was stirred at room temperature for 1 h to obtain a clear sol. Chemically cleaned and dried microscope glass slides of dimension 2 cm × 2 cm × 2 cm were dipped into this sol and drawn at a speed of 1 mm/s. This resulted in the formation of transparent films with thickness of ~5 μ m. Two metallic electrodes (aluminum as cathode and silver as anode) with sharp edges were placed on the surface at a separation of 3 mm. A direct current (DC) voltage (ranging from 5 to 60 V) was applied between the electrodes for approximately 20 s at room temperature. Current through the circuit increased abruptly to a value of a few milliamps. This indicated formation of metallic channels due to the electrodeposition process.

Optical micrographs of the structures generated by the above treatments were taken in a Leitz Laborlux 18 Pol S optical microscope in the transmission mode at magnifications ranging from 500 to 1000. An atomic force microscope (AFM) of Park Scientific Instruments, USA, was used to delineate the structure. The detailed surface morphology was also studied by FESEM (JEOL, JSM-6700F). The microstructure of the electrodeposited pattern was studied by a JEOL 2010 transmission electron microscope.

Results and Discussion

Parts a, b, and c of Figure 1 are the optical micrographs of specimen no. 2 in which fractal, dendritic, and stringy growth of metal were induced by applying a DC voltage of 5, 25, and 40 V, respectively. From these three images it is clear that the transition of morphology is possible by changing the growth voltage, i.e., the deposition rate. For this particular sample (specimen no. 2) fractal to dendritic transition is possible when deposition voltage crosses 15 V. These dendritic structures can also be changed to one-dimensional stringy structure when the voltage increased above 35 V, i.e., at a very high deposition rate.

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Figure 1. Optical micrographs with metal growth in gel specimen of composition $30Zn(NO_3)_2$, $70SiO_2$ under different applied voltages. (a) 5 V, (b) 25 V, (c) 40 V.

The fractal dimension of the ramified structure (Figure 1a) was calculated by a method described earlier.⁶ The value obtained is 1.82. This is a consequence of the generalized diffusion-limited growth mechanism. Figure 2 shows the AFM



Figure 2. AFM micrograph of the structure shown in Figure 1a.



Figure 3. Transmission electron micrograph for the sample corresponding to Figure 1a.

micrograph of the fractal structure, which was shown in Figure 1a. From this image it is evident that nanoparticles form the fractal structure. Figure 3 gives the transmission electron micrograph for the sample. The diameters observed are in conformity with the AFM picture. In high-resolution observation (Figure 4), it is found that there is no correlation of crystal planes among the neighboring particles, which indicates there is no preferred growth direction. This means there is no long-range ordering among the nanoparticles. Figure 5 gives the histogram of particle sizes. The data were fitted by a log-normal distribution function, and the extracted values of mean diameter and standard deviation are 10.5 nm and 1.1, respectively. Average particle size depends on the amount of silica present in the film. Table 2 summarizes the average particle diameter and the geometrical standard deviation. It is seen that the mean diameter of Zn nanoparticles increases as the concentration of Zn²⁺ in the precursor sol is increased.

In the case of dendritic growth TEM images show that there is a variation of particle size and particle distribution with respect to growth voltage. Table 3 summarizes the variation of the average particle size and their distribution with voltage for speci-



Figure 4. HRTEM for sample corresponding to Figure 3.



Figure 5. Histogram of particle sizes as obtained from Figure 3.

 TABLE 2: Average Particle Diameter and the Geometrical

 Standard Deviation for Different Specimen

specimen no.	growth voltage (V)	mean diameter (nm)	standard deviation
1	5	5.2	1.0
2	5	10.5	1.1
3	5	16.5	1.1
4	5	20.2	1.0

 TABLE 3: Average Particle Diameter and the Geometrical

 Standard Deviation for Different Growth Voltage

specimen no.	growth voltage (V)	mean diameter (nm)	standard deviation
2	20	10.0	1.0
2	30	9.2	1.0
2	40	8.5	1.1
2	50	7.8	1.1

men number 2. Figure 6 shows the HRTEM images for specimen 2 with growth voltage 25 V. This lattice image shows that the orientation of neighboring particles is the same, which is a $(10\overline{10})$ plane. This indicates that the particles had grown



Figure 6. HRTEM for specimen no. 2 with a growth a growth voltage of 25 V.



Figure 7. Selected area electron diffraction pattern obtained from Figure 6.



Figure 8. Scanning electron micrograph of specimen no. 2 with metal growth carried out at 25 V.

in a direction perpendicular to the *c* axis of hexagonal closed packed (hcp) zinc crystal. The latter implies that the stackedplane structure is the microscopic source of the anisotropy, which forms the micrometer-ranged dendritic structure of Zn. The selected-area electron diffraction (SAED) pattern (Figure 7) taken from the image position of Figure 6 shows a singlecrystalline structure. The diffraction pattern indicates that the dendrite is oriented perpendicular to the (0002) plane with the three branches along the [1010] (or [100]), [1100] (or [110]), and [0110] (or [010]) directions.^{7–8} Figure 8 is the FESEM image of these dendritic structures. From this image it is seen that the growth is confined in a particular direction and mini



Figure 9. X-ray diffractogram of specimen no. 2 with metal phase grown at different voltages (a) 25 V, (b) 30 V, (c) 40 V.



Figure 10. Schematic representation of the six crystallographically equivalent directions of hcp Zinc.

branches are at 60° angles on both sides of the former. But in the case of the stringy structure, the side branching totally disappears. This implies that it does not get sufficient time for the side branching due to very high growth rate and the growth is confined only in the [1010] direction.

This phenomenon was also observed during XRD investigation. The XRD patterns (Figure 9) show the phase structure and crystal orientation of the Zn nanparticles. Parts a, b, and c of Figure 9 are the XRD patterns of specimen no. 2 with growth voltages 25, 30, and 40 V, respectively. Parts a and b of Figure 9 show that there are two Zn peaks in the XRD spectra, with the highest at the (0002) crystal plane and another lower peak at the $(10\overline{1}1)$. In Figure 9c there is only one peak, which corresponds to the (0002) plane. By comparison of all these figures, it is clear that the second peak is reduced with the increase of growth voltage and completely disappears when the growth rate is very high. This indicates that the (0002) planes of zinc nanoparticles are highly oriented and parallel to the glass substrate.¹⁰ From these results it can be concluded that there exists a preferred growth direction,9 which is normal to the (0002) crystal plane of the Zn nanoparticle arrays. By normalizing the peak areas to the peak intensities of a polycrystalline bulk Zn standard,¹¹ it is found that more than 95% of the Zn nanoparticles in the arrays are oriented along a direction perpendicular to the (0002) crystal plane.

The formation of the dendrites could be explained by the following representation. Metallic Zn has an hcp crystal structure, which indicates that the $(10\overline{1}10)$ planes have six equivalent directions (Figure 10). These directions are ([10\overline{1}0], ([1\overline{1}00], and ([01\overline{1}0]. For spatial confinement, one of the



Figure 11. Schematic representation of proposed formation of the micropine dendritic structure of zinc. (a) Fast growth along $[10\overline{1}0]$ direction. (b) Subsequent side-branch growth alone $[0\overline{1}10]$ and $[1\overline{1}00]$ directions. (c) Further growth of minibranches.

directions, for example, $[10\overline{1}0]$, initiates the growth along the electric field direction and forms a needle in the direction of $[10\overline{1}0]$. Because of the electric field, growth of the dendrite in this direction is much faster than along the other directions (Figure 11a). Subsequent growth along the other two crystallographically equivalent directions $[01\overline{1}0]$ and $[1\overline{1}00]$, leads to the formation of symmetric branches on both sides (Figure 11b). With further growth, all of the branches become thicker and finally interconnected (Figure 11c) and form the micropine dendrite structure as observed in Figure 1b.

Now the question is why the six $\langle 10\bar{1}0 \rangle$ directions are the directions of fastest growth? For electrochemical deposition, new grains will grow if the size of the initial grain exceeds a critical grain size (N_c). The critical dimension N_c for a 2D-like growth is expressed as¹²

$$N_{\rm c} = \frac{bs\epsilon^2}{\left(ze\eta\right)^2} \tag{1}$$

where s, ϵ , z, and b are the area occupied by one metallic atom on the surface of the nucleus, the edge energy, the effective electron number, and a constant, respectively.

 η is the overpotential and is defined as

$$\eta = E(I) - E_0 \tag{2}$$

where E(I) and E_0 are the external current-induced potential and the equilibrium potential of the electrode (potential in the absence of the external current), respectively. From the equation it is clear that in the present case for a particular growth voltage, ϵ is the only parameter, which can control the growth of a new nucleus. This means the low-surface-energy grains grow faster than do the high-energy grains. The rapid growth of the lowsurface-energy grains at the expense of the high-energy grains results in an increase in grain size. So the low-surface-energy facet appears more easily during the deposition. For Zn metal, the $\{1010\}$ surfaces are the most densely packed, so the (1010)planes are the surfaces of lower energy than the (0002) planes. Hence the $(10\overline{10})$ planes are the energetically most favorable surfaces for hcp Zn and the formation of the {1010} facets on the Zn particle surface is expected more than the $\{0002\}$ facets. It is therefore believed that this anisotropy is the reason growth takes place along the $[10\overline{1}0]$ direction. At the same time, the formation of side branches dominated by the $[01\overline{10}]$ and $[1\overline{100}]$ directions takes place. In case of a stringy pattern, the side branching disappears due to very high growth in [1010] direction.

The above discussion indicates that the growth of zinc phase is taking place in a two-dimensional space. To confirm this,



Figure 12. Variation of log(conductance) as a function of log(angular frequency) in precursor gel film of composition 30 Zn(NO₃)₂, 70 SiO₂.

 TABLE 4: High-Frequency Slopes of These Curves Were

 Estimated from Figure 12

temperature (°C)	slope
20	0.48
30	0.48
40	0.52

we have carried out alternating current conductance measurements as a function of frequency on the precursor film containing Zn²⁺ ions in a silica gel. For this silver paint electrodes were applied on the film surface at a separation of 1 mm. Figure 12 shows the variation of log(conductance) as a function of log-(angular frequency) at three different temperatures. The highfrequency slopes of these curves were estimated and are summarized in Table 4. It can be seen that the slope ≈ 0.5 . This is also constant over the temperature range measured. It has been shown earlier that there is a relationship between the high-frequency limiting slope *n* and the shape exponent β appearing in the Kohlrausch–Williams–Watts stretchedexponential relaxation function.¹³ The relation is given by

$$n = 1 - \beta \tag{3}$$

We therefore obtain a β value around 0.5. This suggests that the charge motion occurs in a two-dimensional structure. This result is consistent with the mechanism of zinc pattern formation discussed earlier.

Conclusions

In summary, we have described an experiment in which a stable pattern formation of zinc nanoparticles is possible inside silica film. This pattern can be changed from fractal to dendritic and dendritic to stringy only by changing the growth voltage. For dendritic and stringy structure anisotropy in nanoscale causes the structural transformation.

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