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Optimal Parameters for Synthesis of Magnetic Nanowires in Porous Alumina Templates

Electrodeposition Study

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We have carried out a systematic study of the electrodeposition process to understand the effect of varying three important quantities on the synthesis of nanowires inside porous alumina templates. We have electrodeposited iron nanowires inside porous alumina to determine the optimal settings of these variables to induce effective and efficient nanowire growth. First, we vary the pH of the electrolyte solution to show that pH has little effect on the deposition rate. Second, we vary the magnitude of the applied ac voltage to show that the deposition rate increases with increasing voltage. Finally, we vary the frequency of the applied ac voltage to show that there are three distinct regions corresponding to different deposition rates. We have studied the magnetic properties of the synthesized nanowires and our results as a function of fabrication parameters are discussed. © 2007 The Electrochemical Society. [DOI: 10.1149/1.2509685] All rights reserved.

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Fabrication of nanowires through the process of electrodeposition inside porous templates is a well-known and well-used procedure due to both its effectiveness in growing nanostructures and its inexpensiveness. The process of electrodeposition itself has been known for a rather long time. References 1 and 2 provide an excellent background to the subject. Moreover, the fabrication of metal nanowires has been studied in other papers.³⁻⁵ Specifically, iron nanowires have also been studied, for example, in Ref. 6 and 7. However, despite its pervasiveness in nanofabrication, little work has been done to understand the process itself. In order to develop a reliable method for the fabrication of nanostructures using this technique, it is necessary to have a qualitative and quantitative understanding of the electrodeposition process.

Here we undergo a systematic study to understand the effect of the variation of three variables (pH, voltage, and frequency) involved in the electrodeposition process on the average nanowire growth rate. Experiments are carried out by depositing iron into porous alumina templates. First, we examine the effect of changing the pH of the electrolyte solution on the average growth rate of iron nanowires inside the pores. Then, we vary the magnitude of the applied ac voltage and determine its effect on the deposition rate. Finally, we vary the frequency of the ac voltage to show that there are three unique frequency regions corresponding to distinctly differing electrodeposition rates. These varying parameters have a significant impact on the properties of the nanowires that are deposited inside the template. Using the magnetic property as an analytical tool,^{8,9} each region is analyzed and the results are discussed.

Experimental

Porous alumina templates are created by anodizing aluminum foil in 15% sulfuric acid at 10 V for 30 min, which creates well-ordered alumina pores of approximately 10 nm in diameter and 9380 ± 40 nm in length. A Hitachi model SD400 scanning electron microscope (SEM) was used to verify this. The aluminum backing was left intact on the template to act as a contact during deposition. Deposition of iron takes place in a cell, which is schematically drawn in Fig. 1. A circuit is created by immersing the alumina template in an electrolytic solution of 250 mL deionized water, 2.5 g boric acid, and 10.0 g iron sulfate. Electrical leads are connected to an immersed platinum mesh and to the aluminum backing on the template. An ac voltage is applied across the cell using a power supply and the current in the cell vs time information is recorded. The average filling rate is defined as $\Delta L/\Delta t$, the length of the pore divided by the time it takes to fill the pore in units of nanometers/second. The pore is considered to be "filled" when the current vs

time curve ceases to decrease smoothly and suddenly jumps, at which time the pores overflow and a thin film of iron is deposited on the surface of the nanowires.

For the pH experiments, a standard pH meter is used to measure the pH of the electrolyte solution immediately prior to electrodeposition. The pH is lowered by performing successive depositions using the same electrolyte solution. As current passes through the cell, electrons are donated to the solution, causing the concentration of free protons to increase. Also, the pH is lowered through natural oxidation over time. For the voltage experiments, the magnitude of the ac voltage applied across the cell is varied and deposition continues until the pores have been filled. The current vs time curve is analyzed and the time at which the pore becomes filled is recorded. For the frequency experiments, the frequency of the ac voltage is varied and deposition continues until the pores have been filled. The current vs time curve is then analyzed and the filling time is recorded. It is a well-studied phenomenon that in ferromagnets there are preferred alignment directions.¹⁰⁻¹⁶ Specifically in iron nanowires, the structure and anisotropy has been studied.^{6,7} It has been noted that the easy axis is along the length of the nanowires. Therefore, we can determine whether or not we do indeed have nanowires by applying a magnetic field and measuring the magnetization vs applied field behavior. In the case of nanowires, one expects a large perpendicular anisotropy, that is, for applied fields along the axis of the nanowires, we expect the magnetic spins to align easily in the direction of the field. In contrast, for applied field perpendicular to the axis of the nanowires, we expect the wires to align less easily in the direction of the applied field. By comparing the coercivity and shape of the hysteresis curves in the two directions, one can get significant information into the nature of the deposited nanowires. We expect a high coercivity (when the magnetic field is along the nanowire axis) and a low coercivity (when the field is perpendicular

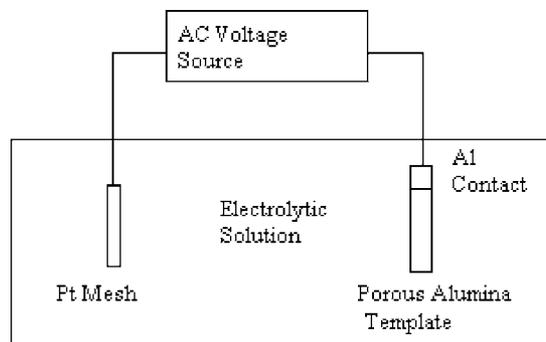


Figure 1. Schematic of the deposition cell.

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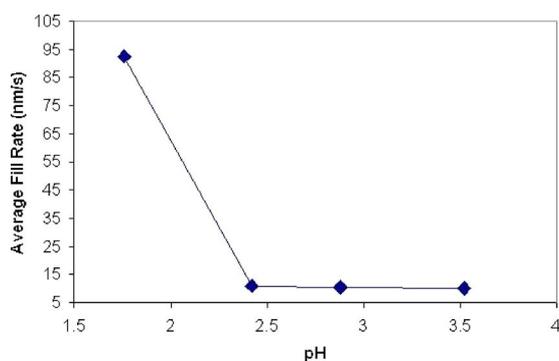


Figure 2. (Color online) Average fill rate as a function of pH of the electrolyte.

to the axis of the wires) would indicate that there is a large perpendicular magnetic anisotropy, thus there are nanowires. Moreover, we can examine the squareness ratio, which can be defined as the ratio of the remnant magnetic field to the saturation magnetization. If there is magnetic anisotropy due to the nanowires, the ratio should be close to 1. These magnetic characterization experiments are done using a Princeton Measurements Corporation MicroMag model 2900 alternating gradient magnetometer (AGM).

pH (results and analysis).— The pH is an important variable in the deposition process because it could be an indirect measurement of the concentration of iron in the solution that is available to deposit. When voltage is applied across the cell, iron from the electrolyte deposits inside the pores. The current in the cell causes some oxidation and the pH increases with increasing deposition time. Clearly, as the concentration of iron in the solution decreases due to deposition, the less likely it is for deposition to occur. So, one can ask, is the pH of the solution directly related to the likelihood that an iron particle will deposit, and thus is it related to the rate of deposition? Figure 2 shows that within a certain range of pH values, the deposition rate is not affected much. As long as one maintains the pH of the solution within a certain range of values, one can expect the same results. However, at low pH values, the rate of deposition is found to sharply increase. This increase is because the current in the cell is very high when the solution is very acidic. We must therefore conclude that the pH of the solution cannot be a good measure of the iron concentration.

Voltage (results and analysis).— The applied ac voltage takes the form of a sine wave, which oscillates between the magnitude of the applied voltage, V_0 . Deposition only takes place during the negative half-cycle. So, we would expect that as V_0 increases, the deposition rate would also increase, as the area under the curve would increase. Figure 3 shows that this is indeed the case. The relation-

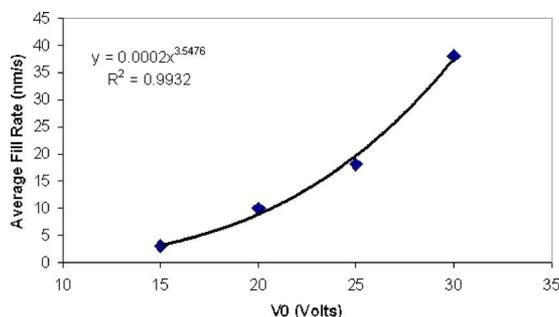


Figure 3. (Color online) Average fill rate as a function of voltage (increases like $x^{3.5}$).

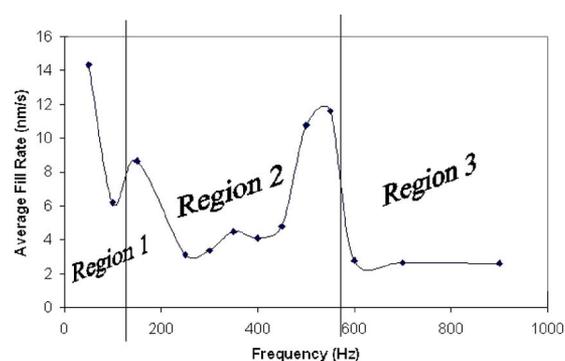


Figure 4. Average fill rate vs frequency (applied voltage 20 V) showing three distinct regions.

ship between the deposition rate and V_0 appears to obey a power law.

Frequency (results and analysis).— The frequency (f) dependence of the average fill rate is the most complicated of all the variables. As was stated before, deposition occurs during a half-cycle of the voltage. So, deposition occurs every $1/2f$ s for a period of $1/2f$ s. As we increase the frequency, the amount of time for deposition per cycle actually decreases. But, concurrently, the number of deposition periods in a length of time increase. It is difficult to predict how this affects the average deposition rate. Figure 4 displays the results where the voltage is kept at 20 V. To better determine the nature of the samples, we have measured the hysteresis loops using an AGM. The magnetic results are displayed in Fig. 5 and 6.

In Fig. 4 we can see three distinct regions. In the first region, there is no real dependence pattern. Here, the frequency is low. If the frequency is low enough, the period of deposition per cycle would be very large. This behavior is almost the same as dc deposition. So,

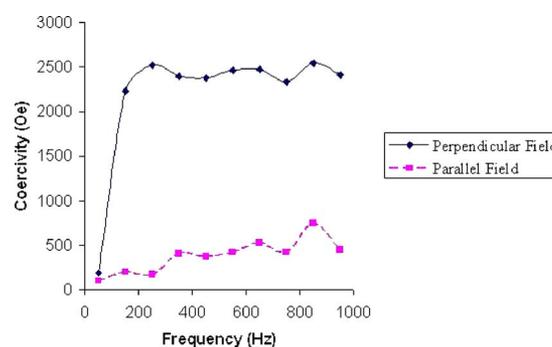


Figure 5. (Color online) Coercivity vs frequency plot for samples in both parallel and perpendicular orientations of the magnetic field.

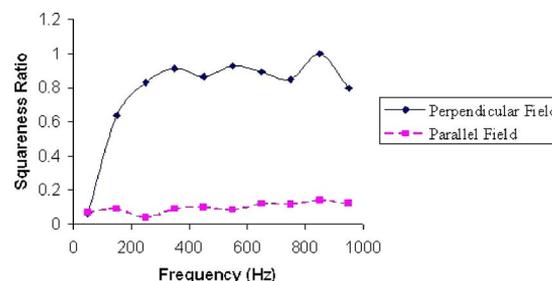


Figure 6. (Color online) Plot of squareness ratio vs frequency for samples in both parallel and perpendicular orientations of the magnetic field.

we can explain region 1 by saying that at a low enough frequency, the deposition acts like dc and very little gets deposited in the pores. Rather, as in dc electrodeposition, a thin film gets deposited on the surface. The deposition rate appears to be rather high because iron is immediately deposited on the surface of the template, causing the current to jump. This explanation is supported by the magnetic measurements that show that the coercivity and squareness ratio are very small for low frequencies, as is expected for thin-film samples.

In region 3, we see an almost constant, slow rate of deposition. Here, the frequency is too large for efficient deposition. The time interval per cycle is too small for adequate deposition to occur. At high frequency, the polarity of the voltage switches very quickly, causing the iron particles to move around a lot but not necessarily deposit, although eventually wires are deposited, as we see in Fig. 5, a high coercivity, and in Fig. 6, a squareness ratio close to 1. However, with such a high frequency, deposition of nanowires proves to be extremely slow.

Region 2 is the ideal region for electrodeposition. Here, one notes a parabolic increase of the deposition rate with frequency. In general, however, one can see an increasing deposition rate with increasing frequency. The existence of nanowires in this region is verified by the magnetic measurements in Fig. 5 and 6.

Conclusion

Despite predictions that the pH of a solution can be used to estimate the concentration of its iron, we find that pH has very little effect on the average deposition rate as long as the pH is within a certain range. We have accurately predicted and explained that an increase in the magnitude of the applied ac voltage increases the average deposition rate. Finally, we have shown that an increasing frequency displays some interesting effects on the average deposition rate. In the region of low frequency, the period of deposition is long, so deposition occurs as dc deposition and only a thin film is deposited. In the region of high frequency, the deposition period does not allow a long enough period for efficient deposition, so the

rate is very slow. The preferred range of frequency values is found in the intermediate frequency region. In this region, the average deposition rate generally increases and nanowires are formed in an efficient manner.

Acknowledgments

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