Vol 13 No 11, November 2004
1009-1963/2004/13(11)/1927-04

Chinese Physics

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Improved liquid–solid–gas interface deposition of nanoparticle thin films

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(Received 14 January 2004; revised manuscript received 19 May 2004)

A liquid–solid–gas interface deposition method to prepare nanoparticle thin films is presented in this paper. The nanoparticles in the part of suspension located close to the solid–liquid–gas interface grow on the substrate under the influence of interface force when the partially immersed substrate moves relatively to the suspension. By using statistical theory of the Brownian motion, growth equations for mono-component and multi-component nanoparticle thin films are obtained and some parameters for deposition process are discussed.

Keywords: interface deposition, nanoparticles, suspension, nanoparticle thin film growth
PACC: 6855, 8115

1. Introduction

In recent years, interest in the preparation and characterization of nanostructure materials has grown constantly because of their distinctive properties and potential applications in technology. Nanotechnology has long had the potential to revolutionize a host of industries. Solid metal nanoparticles have a wide range of applications in optical and electronic devices.[1−4] Prior to integrating various functional nanoparticles into electronic and photonic devices and catalytic reactions, the development of techniques for the precise control of the spatial arrangement of the individual building block on the nanometre and subnanometre levels is crucial to the design and fabrication of advanced components.[5,6] There are many research activities devoted to the development of fabrication methods of thin films with functional properties, such as the chemical deposition method and layer-by-layer self-assembly.[7−12]

In this paper, we present a liquid–solid–gas interface deposition method, namely surface vertical deposition (SVD), to prepare nanoparticle thin films. In principle, this is an ultra-low-speed dip-coating method for nanoparticle thin film synthesis. The nanoparticles in the part of suspension close to the solid–liquid–gas interface deposit on a substrate under the influence of interface force when the partially immersed substrate moves relative to the suspension surface. By using the statistical theory of the Brownian motion, synthesis equations of SVD both for mono-component and multi-component nanoparticle thin films are obtained, and some parameters for film synthesis are discussed. The theoretical results agree with the experiment very well for multi-layer gold nanoparticle thin films reported in our earlier paper.[13]

2. Theoretical analysis

The nanoparticles in suspension near the junction region of three phases, i.e liquid suspension, solid substrate, and air, are the major source for SVD synthesis, and the principle of SVD is demonstrated in Fig.1. The solid–liquid–gas junction region A created by the surface tension of the liquid plays a significant role in SVD because it is the nanoparticles localized there that form the thin films. In region A, the thickness of the suspension near the solid–liquid–gas junction is thinner than the mean-free-path of the nanoparticles, which makes the attraction to the solid the dominant force to be considered in the presented problem. Therefore, the wetting force F leads to the adsorption of nanoparticles on the substrate. When the surface

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of the suspension goes down from the broken line in Fig.1, the nanoparticles in region A will aggregate on the substrate under this force. In SVD the substrate moves relative to the suspension surface as the result of evaporation, so the substrate velocity is much lower than that under normal conditions. In principle, it is an ultra-low-speed dip-coating for preparing nanoparticle thin films. For SVD to succeed, the substrate must be wettable, otherwise the wetting force F will point away from the substrate. Thus in experiments, gold nanoparticle films form on one side of the wettable glass substrate, but do not form on the other side which has been made non-wettable with a wax layer. For our discussion about SVD, three ideal conditions should be mentioned. First, the volume change of suspension is so small that the change of suspension concentration can be ignored. Second, the concentration of suspension is so low that the aggregation of nanoparticles in suspension can be ignored. Third, the size of nanoparticles is so small that the influence of gravity can be ignored.

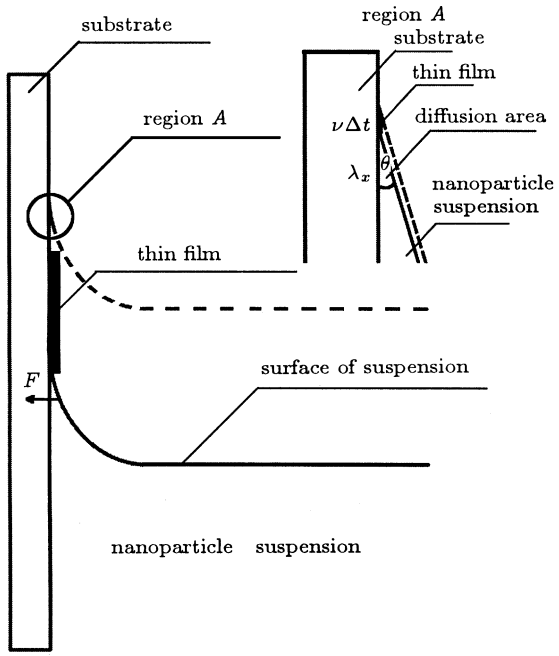


Fig.1. The principle of the Surface Vertical Deposition (SVD).

By using statistical theory for the Brownian motion, the growth equation of density can be obtained. When the suspension surface of the junction region moves downward relative to the substrate with velocity v in small time interval Δt, the area change, which will be the area of thin film formed on substrate, is $\Delta S = Lv\Delta t$, where L is the width of substrate immersed in the suspension. The density, which is the number of nanoparticles in unit area of thin films, is given as

$$N = \frac{\Delta n}{\Delta S} = \frac{\Delta n}{Lv\Delta t}, \tag{1}$$

where Δn is the number of nanoparticles deposited on the thin film ΔS from the nearby volume $V_{\rm Diff}$ of the suspension in time interval Δt, which is caused by the diffusion of nanoparticles. For the Brownian motion, Δn is the number of nanoparticles which grow on the thin film in the diffusion volume $V_{\rm Diff}$, and it is given by

$$\Delta n = KN_{\rm A}V_{\rm Diff}C, \tag{2}$$

where $N_{\rm A}$ is the Avogadro number, C is the concentration of nanoparticles in the suspension and K is the growth coefficient for SVD, which is defined as the adsorption ratios and is equal to the number of nanoparticles adsorbed successfully on substrate divided by the total number of nanoparticles attempting to be adsorbed. The diffusion of nanoparticles in suspension is caused by the Brownian motion which is a random action, and then statistical theory for Brownian motion is used to describe the diffusion of nanoparticles. Thus, the volume of diffusion area $V_{\rm Diff}$ is given as

$$V_{\rm Diff} = \frac{1}{2}\lambda_x^2\theta L, \tag{3}$$

where θ is the contact angle of suspension surface to the substrate surface, and λ_x is the square root of the arithmetic mean of the squares of displacement of nanoparticles for the Brownian motion. The λ_x^2 is given as[14]

$$\lambda_x^2 = \frac{RT}{N_{\rm A}} \times \frac{\Delta t}{3\pi r\eta}, \tag{4}$$

where T is the temperature of suspension, η is the viscosity of suspension, R is the universal gas constant, and r is the average radius of nanoparticles in suspension. By using the Eqs.(1)–(4), the following growth equation for the density of nanoparticles is obtained:

$$N = \frac{K\theta RTC}{6\pi r\eta v}. \tag{5}$$

When the nanoparticle, substrate, solvent and temperature are definite for SVD, Eq.(5) can be written simply as

$$N = \beta\frac{C}{v}, \tag{6}$$

where $\beta = \dfrac{K\theta RT}{6\pi r\eta}$ is a constant coefficient for a definite set of substrate, solvent and temperature. Equation (6) applies to the mono-component nanoparticle thin film made by SVD. For the multi-component nanoparticle thin film, because each kind of nanoparticles moves randomly and no relationship exists between them, the growth equation can be written as

$$N_n = \beta_1 \frac{C_1}{v} + \beta_2 \frac{C_2}{v} + \cdots + \beta_n \frac{C_n}{v}. \qquad (7)$$

For different kinds of nanoparticles in suspension, the growth coefficients are independent of each other as a result of the random Brownian motion. When they are roughly equal, the component ratio of nanoparticles in the film is determined by the concentrations of nanoparticles in suspension.

3. Discussion

Equation (6) shows that the density of nanoparticles in the film can be controlled by the moving velocity of suspension surface relative to substrate and the concentration of suspension. In our experiments with gold nanoparticles, the density of nanoparticles in the thin film made by SVD increases with the increase of the suspension concentration, and on the contrary with the decrease of the descending velocity of suspension surface.[13]

As to the growth coefficient of SVD, the nanoparticles in the thin film should be attracted by the solid substrate surface, but not bonded by the liquid solvent molecules. Thus, the requirement of kinetic energy for nanoparticles in the thin film is

$$E_{\text{Liquid}} < E < E_{\text{Solid}}, \qquad (8)$$

where E_{Liquid} and E_{Solid} are the bond energy to the liquid solvent in region A and the adsorption energy of the solid substrate surface, respectively, which are determined by the materials of the particle, solvent and substrate. So the growth coefficient K is dominated by the materials of particle and substrate, solvent of suspension, and also by the temperature.

The transmission electron microscopy (TEM) images and the electron diffraction pattern of the gold nanoparticle film made by SVD are given in Fig.2.

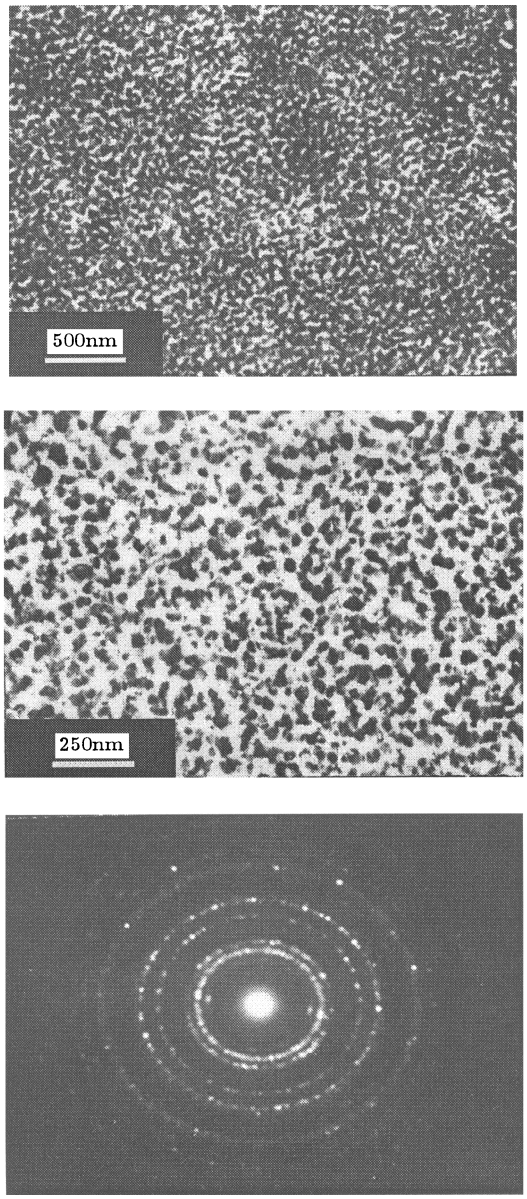


Fig.2. TEM image and electron diffraction pattern of the gold nanoparticle film made by the SVD.

It is shown that the distribution of gold nanoparticles in the thin film is homogeneous and crystalline. This gold nanoparticle film is so thin that it can float on the surface of suspension.

4. Conclusion

Surface vertical deposition, an ultra-low-speed dip-coating method for nanoparticle thin film synthesis, is presented in this paper. The film growth equation for SVD is obtained in this paper by using statistical theory of the Brownian motion. The equation agrees with the experimental results obtained in our earlier reports on multi-layer gold nanoparticle thin films.

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