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Multilayer film deposition of Ag and SiO_2 nanoparticles using a spin coating process

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ABSTRACT

This paper describes the multilayer film deposition of Ag and SiO_2 nanoparticles using a spin coating process combined with ion-sputtering. The Ag-layer thickness was varied from 20 to 80 nm by controlling the Ag concentration in the colloidal solution. Ion-sputtering was found to be a suitable method of surface modification and prevented phase separation during film deposition. The number of layers ranged from one to ten. Cross-section scanning electron microscope images revealed that the deposited multilayer films had laminated structures with high continuity. The optical properties of the prepared multilayer films also were investigated.

1. Introduction

A variety of nanoparticles (e.g., metal, oxide, rear earth fluoride, and so on) have been intensively investigated during the past two decades [1–5]. These materials exhibit very interesting optical, magnetic, and catalytic properties that cannot be realized by the bulk of their counterparts [1,5,6]. Such properties are directly correlated with particle size and shape, inter-particle distance, and the nature of the protecting organic shell [7]. Despite recent advances in nanoparticle characterization, creating nanoparticles with desired properties is a long-standing challenge because manipulating nanoparticles, either individually or collectively, is difficult.

Metal nanoparticles that are deposited as films show unexpected physical properties that are not present in isolated particles. For example, a superlattice of Au nanoparticles can be used in single-electron tunneling devices, which manifest the coulomb blockade phenomenon at room temperature, and also can be used in optical devices [2]. In addition, layer-by-layer films can function as membranes, sensors, magnetic recording media, and photovoltaic devices [8–10]. Typically, metal nanoparticles exhibit characteristic surface plasmon resonance (SPR), which influences the linear and nonlinear optical properties of the sample when it is irradiated by a light source [11]. The SPR characteristics are determined by several physical parameters, such as particle size, the metal fraction in the host matrix (e.g., SiO_2), the nature of the protecting organic shell, and the number of layers [12,13].

Film deposition techniques, including covalent attachment of polymers using conventional coupling chemistry (i.e., Langmuir–Blodgett technique) and electrostatic adsorption of opposite-charged polyelectrolytes, frequently are used to prepare multilayered structures [14]. However, these film deposition techniques not only require long processing times to sufficiently cover the surface, but also demand precise control of the chemical factors such as polyelectrolyte concentration, pH, and hydrogen bonding. Despite the difficulties, these techniques can be used to produce thin nanoparticle layers [8,9,14,15].

Spin coating is a suitable technique for the preparation of periodic films on almost all flat materials. Spin coating has the following advantages: it requires a relatively short manufacturing time; it is cost effective; and, it allows for relatively large surface coverage [16,17]. Moreover, the adsorption and rearrangement of adsorbed materials and the elimination of weakly bonded materials can be achieved simultaneously in short processing times by using high spinning speeds [15]. Different types of solutions, such as those comprised of inorganic complex sols, organic/inorganic macromolecules, and colloidal nanoparticles, have been used as film deposition precursors [5,8,18,19]. However, the film deposition process described above can only be applied to precursors or colloids that are dispersed in either water or organic solvent. In addition, rinsing previously deposited films is a general feature of the repeated film deposition process in the absence of baking.

The present paper describes an effective method for the preparation of multilayered film comprised of two different kinds of nanoparticles (i.e., Ag and SiO_2 nanoparticles) prepared using spin

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coating. Although Ag and SiO_2 nanoparticles have different physical properties (i.e., are hydrophilic and hydrophobic), surface modification with ion-sputtering can prevent phase separation during film deposition. By the spin coating process combined with ion-sputtering, multilayered films comprised of Ag and SiO_2 nanoparticles have been prepared, without a baking step. The approach described in this paper produces multilayered films with laminated structures and without the formation of cracks. The relationship between the optical properties and the number of layers in the multilayered film was systematically examined. The developed film deposition technique described in this paper can be directly applied to the preparation of multi-functional nanoparticle film using various colloidal nanoparticles.

2. Experimental details

2.1. Materials

Monodispersed Ag nanoparticles (NPS-J, Harima Chemicals Inc., Japan) and colloidal SiO_2 nanoparticles (Snowtex XS, Nissan Chemical Industries Ltd., Japan) with mean particle diameters of 5 nm were used as received. Spherical Ag nanoparticles can be readily dispersed in various organic solvents, such as hexane, chloroform, and toluene. Hexane was chosen as the solvent, as well as the dispersant, because of its low viscosity (0.294 cP at 25 °C), low boiling point (68 °C), and relatively low toxicity. A silicon wafer and a glass plate were used as the substrate. Prior to use, both materials were sonicated with acetone for 10 min followed by washing in de-ionized water and ethanol.

2.2. Multilayer film deposition of Ag and SiO_2 nanoparticles using mixed techniques

A spin coating experiment was carried out in a glove box, which included a precision air-conditioning unit (PAU-300S-HC, Apiste Co. Inc., Japan). Based on our previous work, ambient temperature and relative humidity (RH) during the spin coating process are key factors in obtaining complete surface coverage. Temperature and RH were maintained at 25 °C and 60%, respectively, based on previously work by our research group [16]. In addition, a two-step spinning technique was used to produce a uniform particle film over the entire substrate [16,20]. In brief, a cleaned substrate, 1.5 × 1.5 cm, was placed on the spin coater (1H-D7, Mikasa Co. Inc., Tokyo, Japan). Colloidal Ag nanoparticles (20 μL, 60 mg/mL (Ag/hexane)) were dropped onto the center of the substrate by an auto-pipette, and the substrate was spin-coated at 200 rpm for 5 s to spread the dropped hexane solution. The substrate was then rapidly accelerated to 8000 rpm and was spun for an additional 30 s. Prior to deposition of the SiO_2 layer, the previously deposited Ag layer was carefully removed from the spin coater. The Ag-layer surface was modified by sputtering a PtPd layer using an ion-sputtering system (E-1010H, Hitachi, Japan). The details are as follows: (1) the Ag layer deposited on a substrate was placed on a vacuum chamber; (2) the pressure of the chamber was adjusted to 0.05 torr for 150 s; and, (3) a 5 nm PtPd layer was deposited, with pressure, onto the Ag layer for 30 s at 15 mA. During surface modification, sample heating and damage were minimized through the use of ring electrodes and a floating sample stage, indicating that the actual temperature of a substrate was maintained at room temperature or slightly increased. A SiO_2 colloidal solution (50 μL, 100 mg/mL (SiO_2/water)) was dropped onto the surface of the modified Ag film and the spin steps described above were repeated. The film deposition step was repeated until the desired number of layers was obtained. Fig. 1 shows a schematic diagram of the multilayer film deposition of an Ag nanoparticle spin-coated layer, a PdPt sputtered layer, and a SiO_2 nanoparticle spin-coated layer.

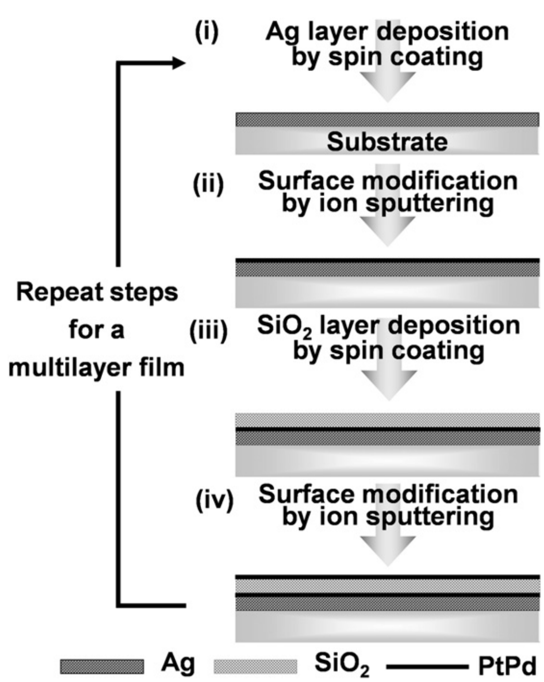

Fig. 1. Schematic diagram of multilayer film deposition of Ag nanoparticle spin-coated layer, PdPt sputtered layer, and SiO_2 nanoparticle spin-coated layer.

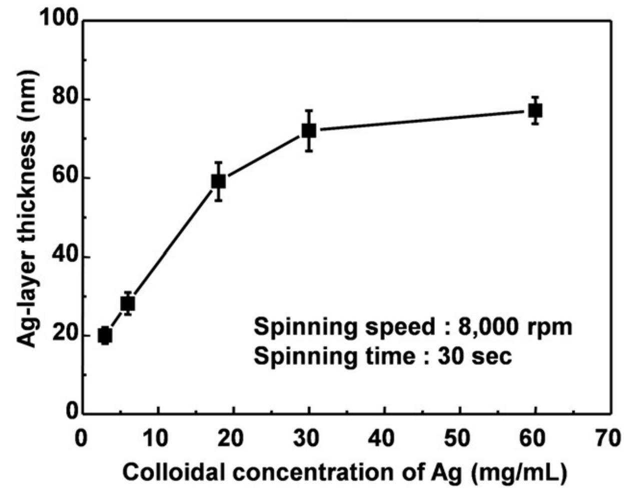

Fig. 2. Ag layer thickness as a function of the Ag concentration in the colloidal solution.

2.3. Film characterization

The morphology and layer thickness of the Ag and SiO_2 nanoparticle films were observed using a field emission scanning electron microscope (FE-SEM, S-5200, Hitachi, Japan) operated at 20 kV. The crystalline phase was characterized by X-ray diffraction (XRD, RINT 2200V, Rigaku Denki, Tokyo, Japan) using nickel-filtered Cu Kα radiation (λ = 1.5408 Å) at 40 kV and 30 mA. The optical properties of the multilayer films were analyzed by measuring the absorbance spectra using a UV–vis spectrophotometer (UV-3150, Shimadzu, Japan). For the analysis of the optical properties, the multilayer films were deposited onto a cleaned glass substrate.

3. Results and discussion

3.1. Ag-layer deposition using the spin-coating process

In general, the thickness of films deposited using the spin coating process can be controlled in the range of tens to several hundreds of nanometers by varying the following parameters: spinning speed and time, ambient humidity and temperature, colloidal concentration, and