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Preparation of nanoparticle-embedded thin films by simultaneous feeding of gaseous and solid raw materials in plasma-enhanced chemical vapor deposition process

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ABSTRACT

Titania (TiO_2) films in which silica (SiO_2) nanoparticles are embedded (SiO_2/TiO_2 films) are prepared by a combination of a novel aerosolization technique and plasma-enhanced chemical vapor deposition (PECVD). Using titanium tetraisopropoxide (TTIP) in a microwave plasma field, anatase films are prepared on silicon and quartz-glass substrates. By utilizing Coulomb explosion of charged droplets in the plasma field, an aerosol with well-dispersed SiO_2 nanoparticles is obtained from the breakup of sprayed droplets of a nanoparticle suspension. Simultaneous feeding of the TTIP vapor as a gaseous raw material and the SiO_2 nanoparticle aerosol as a solid raw material enables preparation of the SiO_2/TiO_2 films with many protrusions. The number and size of the protrusions increase with increasing concentration of the nanoparticle suspension and increasing size of the nanoparticles, respectively. The size of the nanoparticles is related to the surface roughness of the SiO_2/TiO_2 films. Quantitative evaluation of the protrusions suggests that the mechanism of the protrusion evolution on SiO_2 nanoparticles varies with the size of the nanoparticles. Embedding SiO_2 nanoparticles into the TiO_2 films enhances the photocatalytic activities compared to that of a TiO_2-only film probably because the protrusions increase the surface area of the films.

1. Introduction

Nanocomposite films, in which different species coexist on the nanoscale, are of great interest to researchers because of the integrated properties of the species. In particular, thin films in which nanoparticles are embedded have the potential to be used in many applications such as optics [1], electronics [2,3], catalysts [4], sensors [5], anti-bacterial materials [6], and dye-sensitized solar cells [7,8]. In order for any desired properties to emerge, the composition, size, quantity, and dispersion of the nanoparticles must be carefully controlled before they are embedded in the films.

The use of pre-formed nanoparticles is beneficial to the control of size and composition of embedded nanomaterials. Nanoparticle-embedded thin films have generally been prepared by coating a substrate with a matrix solution, in which pre-formed nanoparticles were dispersed, and then drying and heat-treating the coated substrate [9–13]. However, the products of this type of liquid-phase preparation inevitably contain impurities such as solvents and dispersants of nanoparticles. On the other hand, a gas-phase process has the advantage of the ability to prepare thin films with high purity. Recently, processes based on aerosol-assisted chemical vapor deposition (AACVD) were applied to prepare nanoparticle-embedded films [14–19]. AACVD uses an aerosol of droplets of a precursor solution to transport the precursor to the substrate in a CVD chamber. Adding pre-formed nanoparticles to the precursor solution enables transport of the nanoparticles as well as the precursor, allowing nanoparticle-embedded films to be prepared. However this process is limited by the small range of solvents in which pre-formed nanoparticles can be dispersed. Avril et al. improved the AACVD method by separately feeding the precursor of titania (TiO_2) and pre-formed alumina (Al_2O_3) nanoparticles to produce a TiO_2 film that incorporates agglomerated micrometer-sized Al_2O_3 particles [20]. In this process, the pre-formed nanoparticle suspension and precursor solution were sprayed from individual supply lines and simultaneously transported onto a substrate to produce the TiO_2 film with embedded Al_2O_3 particles. However, agglomeration of deposited nanoparticles is inevitable when conventional spray-drying methods [18–21] are used because multiple nanoparticles contained in a single sprayed droplet tend to agglomerate after evaporation of the solvent in the droplet; this always happens except when the number density of nanoparticles is extremely low. Agglomerated nanoparticles with large secondary particle size are not desirable for nanoparticle-embedded films because they tend to degrade inherent characteristics such as surface plasmon resonance and photocatalytic activities of the nanoparticles [22]. Thus,

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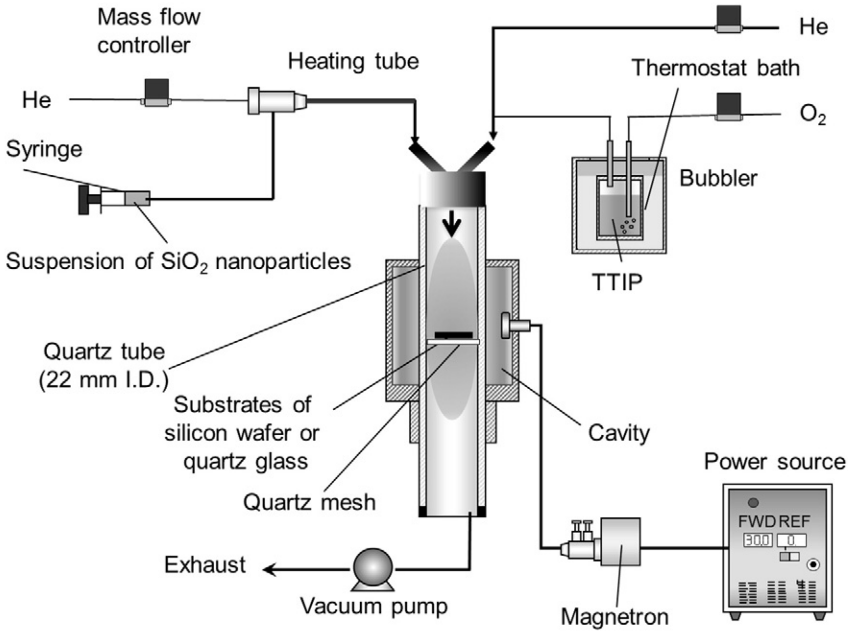

Fig. 1. Schematic of the experimental setup.

a method for preparing nanoparticle-embedded films without agglomeration of the nanoparticles should be developed.

Three years earlier, we developed a new aerosolization technique based on a spray-drying method, which resulted in less or no agglomeration of aerosol nanoparticles with high number density [23]. Droplets sprayed by a pressurized two-fluid nozzle were charged by unipolar ions and then heated to enhance shrinkage, which caused breakup of the droplets by Coulomb explosion. The breakup of the charged droplets generated small droplets containing fewer or single nanoparticles, resulting in less or no agglomeration of the aerosol nanoparticles. Using this concept, we then devised an in-flight coating method of carbon nanotubes (CNTs) in a plasma CVD reactor [24,25]: a CNT suspension was sprayed and fed into the plasma reactor together with vaporized metal–organic precursors. Since a large number of electrons exist in a plasma field [26,27], the sprayed droplets were charged by the electrons. Charging of the droplets caused Coulomb explosions and generated an aerosol of CNTs with less agglomeration. The well-dispersed CNTs were coated with metal oxides by the plasma reaction of the precursor with the airborne CNTs. Thus, we expect that a combination of AACVD and the breakup of droplets by Coulomb explosion would enable the preparation of films containing nanoparticles with less agglomeration.

Most recently, we developed a new plasma-enhanced CVD (PECVD) method for preparing films incorporating well-dispersed nanoparticles; the vaporized precursor and droplets of the nanoparticle suspension were simultaneously fed into a plasma field, and Coulomb explosion was used to generate an aerosol of well-dispersed nanoparticles. Using SiO_2 nanoparticles with various primary particle sizes as a solid raw material and titanium tetraisopropoxide (TTIP) as a gaseous raw material, we prepared TiO_2 films in which silica (SiO_2) nanoparticles were embedded (hereafter referred to as SiO_2/TiO_2 films). We chose SiO_2/TiO_2 films to demonstrate the validity of our latest method not only because SiO_2 and TiO_2 are model thin-film materials, but also because of the prospective enhancement of the TiO_2 film's photocatalytic activities by the embedding of SiO_2 nanoparticles [28]. We first verified the preparation of TiO_2-only films by PECVD and the generation of SiO_2-nanoparticle aerosols with less agglomeration by Coulomb explosion. The SiO_2/TiO_2 films were then prepared by simultaneous feeding of the gaseous and solid raw materials. The structure, morphology, and photocatalytic activity of the SiO_2/TiO_2 films were evaluated. In addition, the evolution of protrusions induced by embedding of the nanoparticles was investigated quantitatively.

2. Experimental

The apparatus used to prepare SiO_2/TiO_2 films, which is shown schematically in Fig. 1, consisted of systems for feeding the gaseous and solid raw materials, microwave supply, plasma generation, and substrate holding. The details of the microwave supply and the plasma generation systems are reported in our previous papers [24,29]. The plasma cavity

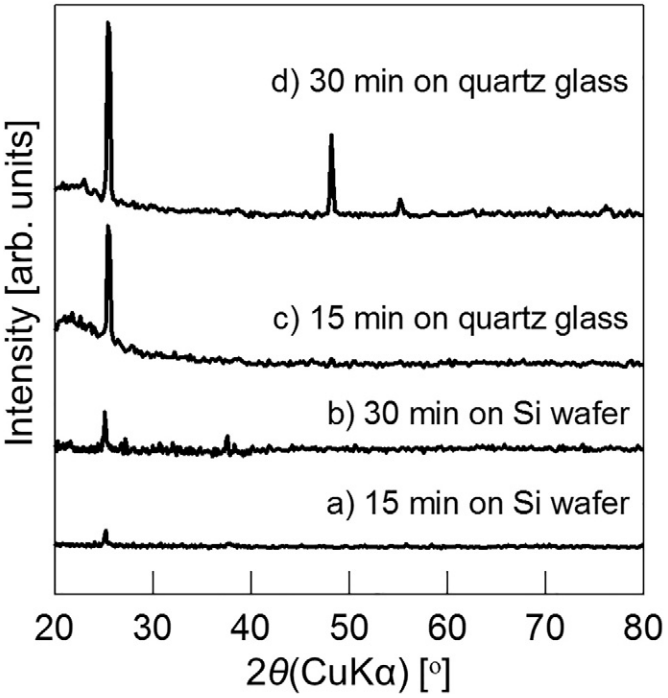

Fig. 2. XRD patterns of TiO_2 films prepared after (a) 15 min and (b) 30 min of deposition on a Si-wafer substrate and after (c) 15 min and (d) 30 min of deposition on a quartz-glass substrate.