Control of ZnO nanoparticle domain in a coaxial gas-flow pulse Ar/O₂ plasma

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Abstract: A limited area, to which ZnO nanoparticles are selectively adhered, is called a domain. Formation of the domain was controlled by using a coaxial gas-flow pulse Ar/O₂ plasma. The formation processes were estimated by SEM and EDX. The particle yield and size in the domain were found to be controlled by changing the experimental parameters. The formation of the domain was closely related to initial surface condition of substrates.

Keywords: ZnO nanoparticle, domain, sputtering, pulse discharge

1. Introduction

Zinc oxide (ZnO) is an n-type semiconductor with a wide band gap of 3.37 eV, a large exciton binding energy of 60 meV, and high thermal and mechanical stability. Therefore, there are many applications of ZnO such as transparent electrodes, light-emitting diodes (LEDs), semiconductor material, and so on.

ZnO nanostructures such as nanorods and nanoparticles showed a definite promise for an employment in nanoscale devices, including field emitters, UV lasers, field-effect transistors, dye sensitized solar cells, and gas sensors. In addition, spherical ZnO nanoparticle was expected for an application to quantum dot solar cells.

In general, ZnO nanorods and nanoparticles have been produced by vapour-liquid-solid (VLS) process, chemical vapour deposition (CVD), and liquid laser melting method. Our group is focusing on a plasma process for the growth of ZnO nanostructures [1]. This process is superior to the other processes for low temperature deposition and large area deposition. Besides, when the energy of plasma is controlled, ZnO thin films or ZnO nanoparticles can be selectively produced. However, very few studies have dealt with energy-controlled plasma.

In this report, formation of ZnO nanoparticles domain was investigated by focusing on its dependence on the surface condition of Si substrate.

2. Experimental apparatus

Fig. 1 shows a schematic of the experimental apparatus [2]. The experiment was performed in a low-pressure plasma by employing reactive ion sputtering. As a source of Zn, a Zn rod electrode was used and installed in a glass tube. The flow rates of Ar and O₂ gases were adjusted by mass flow controllers independently and the mixed gas was introduced into a stainless tube. A square-pulse voltage with pulse width of 5 µs was employed for the plasma production.

Partial pressure ratio of Ar/O₂, pulse repetition frequency and supplied voltage were controlled as a parameter. The substrate used was a Si wafer, the surface of which was cleaned by methanol before the experiment. It was possible to change the gas pressure ratio O₂/Ar, input power and substrate position. The wavelength of the optical emission from the plasma was measured by optical emission spectroscopy (OES). ZnO deposition was analysed by scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS).

3. Experimental results and discussions

The experiment was conducted when O₂ and Ar flow rates were 25 and 25 sccm, respectively, i.e., O₂/Ar = 1/1, and the total pressure was 30 Pa. From the results of OES, the emission spectra of Ar and O₂ were observed, but those of Zn were not clearly observed. Therefore, our experimental condition was in an oxide mode.

In our experiment, the sputtering took place only in a short pulse width of 5 µs. The sputtered ZnO molecules from the electrode would react and coagulate each other, and finally grow as clusters and nanoparticles during the pulse-off time interval.

Fig. 2 shows typical SEM images of the depositions on the Si substrate. As shown in Fig. 2a, many spherical nanoparticles were observed only in a limited area called a domain. Almost no nanoparticles were observed outside the domain. The shape of the domain was quite
irregular and the domain size was in a range of 20 - 200 µm. The size of the domain was enlarged with the discharge time, and finally several domains were merged into one big domain.

Fig. 2. SEM images of (a) nanoparticle domain, and (b) ZnO nanoparticles adhered to the domain area.

As shown in Fig. 2a, it was noticed that the domain was a very special limited area, to which nanoparticles preferentially adhered. Fig. 2b shows SEM image of nanoparticles adhered to the inside of the domain. Typical size of the nanoparticles in the domains was 100 nm, being of fairly uniform. They seemed to be attached to the background layer grown on Si substrate. From EDX analysis, the particle was consisted of only oxygen and zinc. Therefore, it was confirmed that these particles were made of ZnO. Further, as a background layer, many ZnO nanorods were also observed.

It was well known that these nanoparticles were negatively charged and trapped electrostatically in the plasma for a long time for their growth. Variation of the density and size of nanoparticles adhered to the inside of the domain was shown in Fig. 3 as a function of applied voltage. It could be seen that the particle density markedly increased with an increase of the applied voltage. But, the particle size was not much increased. This result implied that the number of particles produced depended on amount of sputtering that was enhanced by the applied voltage. However, the size of nanoparticles, growing and levitating in the plasma, was determined strictly from the balance of forces acting on the charged nanoparticles. The nanoparticles with the other size were supposed to be detrapped and finally eliminated from the plasma space.

Fig. 3. Density and size of ZnO nanoparticles adhered to the inside of domains.

In order to verify formation mechanism of the domain, surface cleaning process using methanol was changed. Fig. 4 shows SEM image of a self-organized circular-shape domain, to which many nanoparticles were preferentially adhered. We could also find some nanoparticles arranged in lines. These results implied that the nanoparticles could adhere only to a limited circular area cleaned by methanol nanodroplets, and/or could adhere to the stripes wiped. The change of surface condition due to the cleaning process might cause some patterning for the growth of background nanorod layers, which would then give rise to patterning of surface charges for the selective adhesion of charged nanoparticles, just like a copy machine.

Fig. 4. SEM image of self-organized circular-shape domains, to which nanoparticles were selectively adhered. Some particles were arranged in lines.

4. Conclusion

We focused on the domain formation of ZnO nanoparticles in Ar/O₂ plasmas. The domains could provide only a limited area for the nanoparticles adhesion. The size and shape of the domain were quite irregular. However, various shape of domains would be controllable by patterning the substrate surface before the deposition.
Our sputtering system was quite effective for controlling nanoparticle adhesion only to the inside of a limited and selected area called a domain.

5. References