Generation control of ZnO nanoparticles using a coaxial gas-flow pulse plasma

同軸ガス流型パルスプラズマを用いた ZnO ナノ粒子の生成制御

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Generation of ZnO nanoparticles was investigated using a coaxial gas-flow pulse plasma. We studied how zinc atoms, sputtered from a zinc target, reacted with oxygen in a plasma and/or on a substrate to form ZnO nanoparticles when the discharge parameters, such as gas flow rate ratio, substrate position, and input power, were controlled in an O_2/Ar plasma. The formation processes were estimated by SEM and EDX. We observed many nanoparticles of ZnO deposited in a limited area called domain. The particle yield and size was found to be controlled by changing the experimental parameters. The diameter of the particles was typically 100-200 nm.

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) or semiconductor material and so on.

ZnO nanostructures such as nanorods and nanoparticles showed a definite promise for an employment in nano-scale 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 vapor-liquid-solid (VLS) process, chemical vapor 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, the formation of ZnO nanoparticles was investigated by focusing on its dependence on the discharge parameters such as input electric power and pulse repetition frequency.

2. Experimental setup

Figure 1 shows a schematic of 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 (diameter 2 mm) was used and installed in a glass tube. The flow rates of Ar and O_2 gases were adjusted by mass flow controllers independently and the mixed gas was introduced into a stainless tube. A pulse voltage with pulse width of 5 μs was employed for the plasma production.

Partial pressure ratio of Ar/O_2, pulse repetition frequency and supplied voltage were controlled as a parameter. The substrate used was a Si wafer. It was possible to change the gas pressure ratio O_2/Ar, input power and substrate position. The wavelength of the optical emission from the plasma was measured by optical emission spectroscope (OES). ZnO deposition was analyzed by scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX).

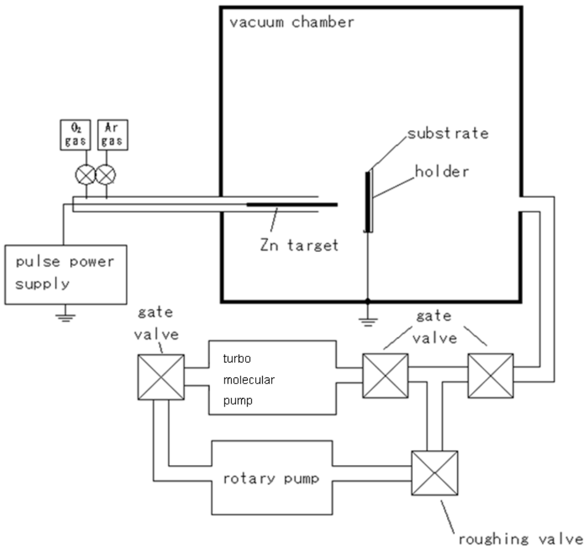

Fig.1 Schematic of experimental apparatus

3. Experimental results and discussion

The experiment was conducted when O_2 and Ar flow rates were 25 and 25 sccm, respectively, i.e., O_2 /Ar = 1/1, and the total pressure was 30 Pa. From the results of OES, the emission spectra of Ar and O_2 were observed, but those of Zn were not observed. The results implied that our experimental condition was in an oxide mode.

Figure 2 shows a typical SEM image of the depositions on the Si substrate. Many spherical nanoparticles were observed only in limited area called domain. The shape of the domain was quite irregular and the domain size was in a range of 20-200 μm. On the other hand, the particles in the domains were typically 100 nm, being of fairly uniform. 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.

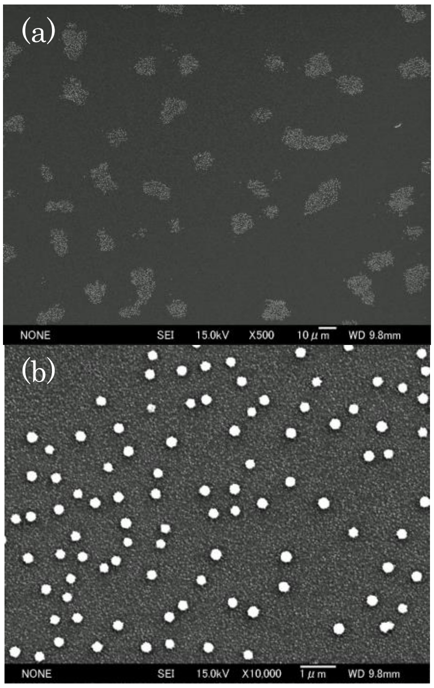

Fig.2 (a) Nanoparticle domains formed on Si substrate and (b) nanoparticles inside the domain

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 to clusters and nanoparticles during the pulse-off time interval.

Figure 3 shows the density and size of the particles as a function of applied voltage. It can be seen that the particle density greatly increased with an increase of applied voltage. But, the particle size was not much increased. This result implied that the number of particles depended on the amount of sputtering that was enhanced by the applied voltage. But, the size of the particles, growing and levitating in the plasma, did not strongly depend on the applied voltage.

In order to verify the relation between the particle size and pulse-off time interval, the pulse repetition frequency was changed. As shown in Fig. 4, the particle size was found to become smaller by increasing the pulse repetition frequency. The reason is considered as follows: by shortening the pulse-off time interval, particle aggregation time in the space is reduced and then the particle growth was obstructed.

It is also noted that the particles can be regularly arranged in the domain under certain conditions.

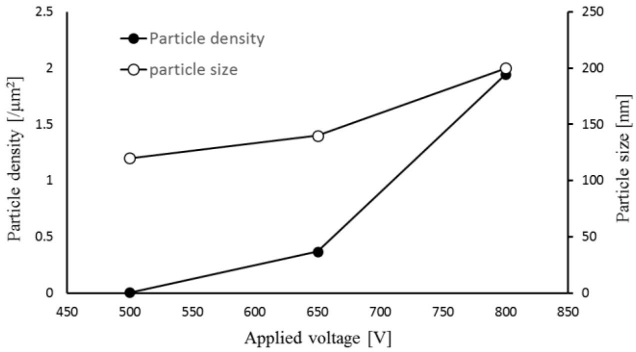

Fig.3 Applied voltage dependence of particle density and particle size.

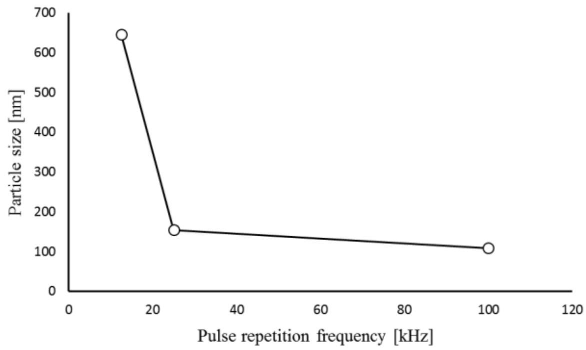

Fig.4 Particle size as a function of pulse repetition frequency.

4. Conclusion

We focused on the formation of nanoparticles in Ar/O_2 plasmas. The size of nanoparticles was in a range of 100-200 nm. From EDX analysis, these nanoparticles were made of ZnO. The number of ZnO particles can be controlled by applied voltage. On the other hand, the size of ZnO particles can be controlled by pulse repetition frequency.

References

[1]K.Kumeta et al.,Thin Solid Films, **518** (2010) 3522.
[2]H.Shirahata et al., Int. Conf. Reactive Plasma ICRP-8/SPP-31, 5P-AM-S05-P18, 2014.