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Effect of radical assist using atmospheric pressure plasma jet for synthesis of zinc oxide thin film by mist CVD

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Zinc oxide (ZnO) is a wide band gap semiconductor having a band gap of 3.37 eV. Because of its high conductivity, high transparency to visible light, and abundant material resources, applications such as transparent conductive film, light emitting elements, etc. are expected.[1] ZnO thin films have been deposited using various techniques, such as magnetron sputtering, reactive evaporation, pulsed laser deposition (PLD), metal organic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE), spray pyrolysis, sol-gel method, and mist chemical vapor deposition (CVD) [1]. However, it is difficult for the conventional ZnO deposition processes to achieve high-rate and low-temperature deposition at the same time. The mist CVD is a method of film deposition realized by thermally-decomposing a mist-like solution containing a raw material to form a thin film. Using the method, a thin film can be formed on a large area with a high process speed under atmospheric pressure [2]. However, there is a problem of its high deposition temperature. In order to solve this problem, we considered to perform film formation assist using atmospheric pressure plasma jet (APPJ). APPJ has a potential to realize high density plasma with low gas temperature under atmospheric pressure, and is enable us to generate a large amount of radical species [3]. It is thought that reactive species generated by the APPJ cause activation of mist particles. In this study, in order to the reduction of the film formation temperature in addition to the quality improvement of the thin film synthesized by the mist CVD method, the effect of oxygen radical generated by the APPJ on the film formation in the mist CVD have been investigated.

An APPJ was generated by applying a high-frequency voltage pulsed at 18 kHz with a peak-to-peak voltage of 12 kV to an electrode in a quartz tube with an inner diameter of 4 mm, flowing a mixture gas of Ar and O_2 gases. Although the flow rate of Ar gas was fixed at 1.5 L/min, the O_2 gas flow rate was change from 0 to 4.5 sccm in order to investigate the effect of oxygen radical on the film formation. The APPJ source was set in a process chamber purged by N_2 gas at the flow rate of 2.5 L/min and the pressure inside the chamber was kept at atmospheric pressure. A mist particles of a H_2O solution containing zinc acetate ($Zn(CH_3COO)_2$, Concentration: 0.01 mol/L) formed by an ultrasonic element were supplied to on a Si substrate with a N_2 carrier gas at the flow rate of 2.5 L/min as the ZnO source. The growths of ZnO film were carried out on the Si substrate set on a stage heated at 400°C. The processing time of film formation was fixed at 30 minutes. The surface morphologies and cross sectional structures of the ZnO thin films were observed by a scanning electron microscopy (SEM).

Figure 1 shows the top view and cross section SEM images of the ZnO thin film grown without radicals assist (a) and with radical assist in the conditions of (b) O_2 gas flow rate: 0, (c) 1.5, and (d) 4.5 sccm. Comparing (a) and others in Fig.1, it was found that the thickness of film grown with radical assist was approximately two times higher than that without radical assist. Furthermore, the particle size increased. From the above, it was suggested that the growth rate of film was improved by radical assist. However, in the radical assist mist CVD, the surface roughness of the grown film was very large. Comparing (b) and (c) in Fig.1, the supply of O_2 gas changed the shape of particle synthesized by the the radical assist mist CVD from a sharp to a round one. In addition, comparing (c) and (d) in Fig.1, the film surface became relatively flat with the increase in the O_2 gas flow rate. The amount of oxygen radicals supplied from APPJ changes as the flow rate of O_2 gas to APPJ increases. Therefore, it is found that the oxygen radicals generated by the APPJ contributes to the surface morphology and structure of ZnO thin film grown by the mist CVD.

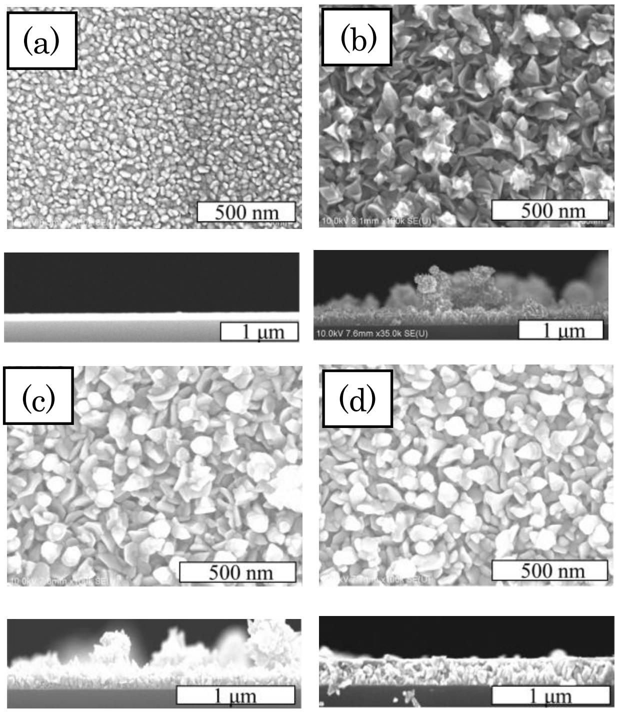

Fig. 1 The top view and cross section SEM images of the ZnO thin film (a) without radicals assist, (b) O_2:0 sccm, (c) O_2:1.5 sccm and (d) O_2:4.5 sccm.

References
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