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Formation of ZnO Films by Plasma-Assisted Mist-CVD Using $Zn(CH_3COO)_2$

酢酸亜鉛を用いたプラズマ支援ミストCVDによる酸化亜鉛薄膜の形成

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Mist-included high-density RF plasma source has been developed for low temperature and high rate deposition process of zinc oxide films. For the deposition of a zinc oxide, the inductively coupled RF discharge was generated with injection of mists including metallic salt of zinc. Zinc oxide (ZnO) film by plasma-assisted mist-CVD using $Zn(CH_3COO)_2$ have been reported and effects of the plasma exposure on film properties. Zinc oxidize films deposited by mist CVD assisted with argon/oxygen mixture plasma have showed existence of the crystallized zinc oxide films.

1. Introduction

Zinc oxide (ZnO) which has a wide- direct band gap of 3.37 eV, is a very attractive material for optical and electrical devices, such as ultraviolet emitters and detectors, transparent conducting electrodes, heterojunction transistors, thin film transistors and sensors[1-3]. ZnO films have been grown by various techniques including magnetron sputtering [4], chemical vapour deposition [5], pulsed laser deposition [6] and molecular beam epitaxy [7]. However, deposition of zinc oxide via conventional methods involves problems associated with low deposition rate. To overcome this problem, plasma-assisted mist CVD method has been developed for low temperature and high rate deposition process of ZnO films. In this presentation, the experimental results regarding zinc oxide film deposition with plasma-assisted mist-CVD using $Zn(CH_3COO)_2$ deposition method have been reported and effects of the plasma exposure on film properties.

2. Experimental

Schematic diagram of experimental setup for the plasma-assisted mist-CVD is shown in Fig.1. A water-cooled copper coil antenna (three turns) was looped around alumina discharge tube of 50 mm in outer diameter and 42 mm in inner diameter. The antenna is coupled to a 1000 W RF power generator at 13.56 MHz via a matching network. Air and argon gas were supplied from upstream of the stainless tube of 18 mm in outer diameter and 15 mm in inner diameter. In this study, the $Zn(CH_3COO)_2$ solution was used for zinc oxide source. The supply of the $Zn(CH_3COO)_2$ solution was performed by ejection of droplets of $Zn(CH_3COO)_2$ solution from a nozzle in the vacuum chamber. The total pressure was kept constant at 50-100 Pa. The Si and glass substrates were located in the downstream region at 250 mm from the copper coil antenna.

Plasma density was measured with a cylindrical Langmuir probe. Crystalline structure of zinc oxide films was analyzed with X-ray diffraction. Surface properties of zinc oxide films were studied with a scanning electron microscope (SEM).

3. Results

To investigate characteristics of plasmas for plasma-assisted mist-CVD of zinc oxide films, plasma density for argon gas (Ar 100%) at a distance of 195 mm from the antenna was measured. Figure 2 shows RF power dependence of the argon plasma density with total pressure as a parameter.

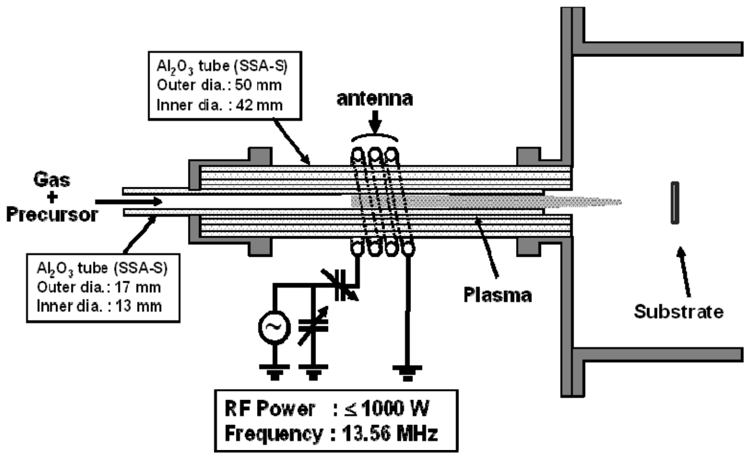

Fig.1. Schematic diagram of experimental setup for the plasma-assisted mist-CVD

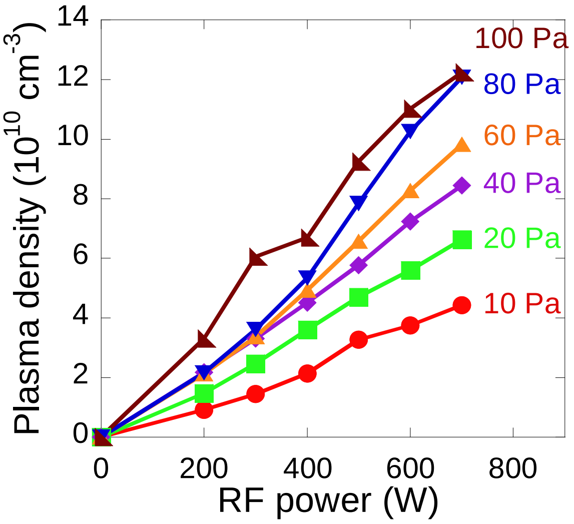

Fig. 2 Variation of plasma density on RF power as a parameter of pressure.

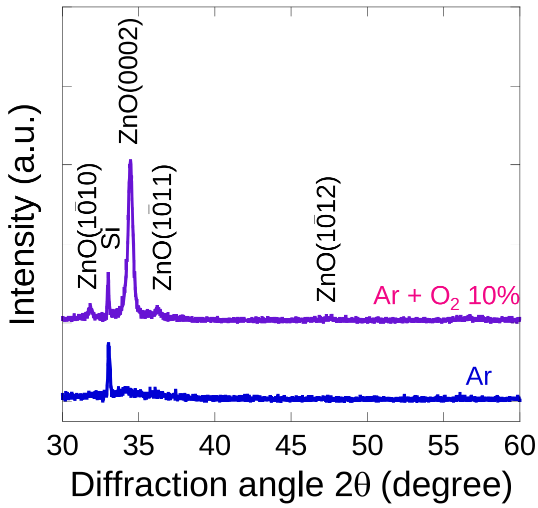

Fig. 3. XRD patterns of films deposited with irradiating Ar plasma and Ar+O_2 (10%) mixture plasma.

With increasing RF power, the argon plasma density linearly increased at all the conditions of total pressure. The results also show that the increasing in plasma density depended on the increasing in total pressure. The argon plasma density became as high as 1.2 x 10^{11} cm^{-3} at 700 W at 1000 Pa. From the viewpoint of an efficient deposition, it is desirable that the plasmas for deposition of ZnO films are high-density. The result indicates that high-density plasmas as high as 10^{10}-10^{11} cm^{-3} can be obtained using plasma-assisted mist-CVD.

Surface properties of zinc oxide films were studied with an X-ray diffraction (XRD). Figure 3 shows XRD patterns of zinc oxide films using pure argon and argon/oxygen mixture plasmas (oxygen flow ratio 10%) exposure to droplets of $Zn(CH_3COO)_2$ solution. As shown in Fig. 3, XRD patterns of zinc oxidize films with argon/oxygen mixture plasma exposure have showed the XRD results showed the XRD results showed evident peaks of ZnO(0002), indicating that highly c-axis oriented films were grown, and small peak of ZnO(10$\bar{1}$0), ZnO(10$\bar{1}$1) and ZnO(10$\bar{1}$2). These results suggest that the ZnO deposited with argon/oxygen mixture plasma assisted mist CVD method shows the highly c-axis-orientation. Figure 4 shows SEM images of surface morphologies of ZnO films deposited by plasma-assisted mist-CVD as a parameter of oxygen flow ratio. The ZnO films for argon/oxygen mixture plasma exhibited columnar growth on the round gains.

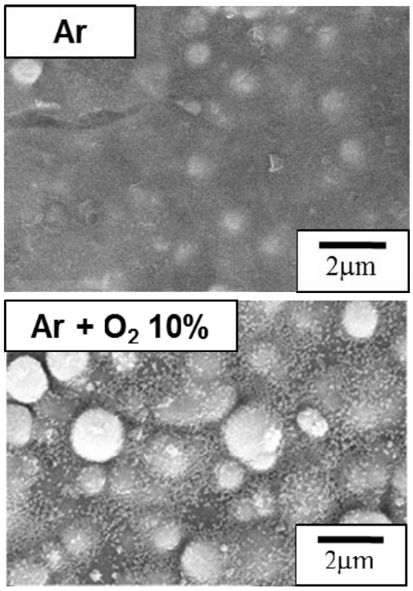

Fig. 4. SEM images of ZnO films deposited with irradiating Ar plasma and Ar+O_2 (10%) mixture plasma.

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