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Preparation of ZnO Film by Photo Atomic Layer Deposition

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Low-resistivity textured ZnO films were grown by photo atomic layer deposition (photo-ALD) technique using diethylzinc (DEZ) and H_2O as reactant gases. It was found that the average growth thickness per growth cycle was in good agreement with the ZnO monolayer thickness in certain region of the substrate temperature. Moreover, the resistivity of the films grown with UV irradiation was one order of magnitude less than that grown without UV irradiation. The minimum resistivity of 6.9×10^{-4} Ω cm was obtained by photo-ALD method without any intentional doping.

1. INTRODUCTION

Recently, ZnO has become attractive for a-Si and $Cu(InGa)Se_2$ solar cells as transparent front and rear contacts, because of its low growth temperature and its high stability in hydrogen plasma. We have established the growth of textured and low resistivity ZnO films by using the MOCVD and photo-MOCVD techniques [1, 2]. The films have been applied to the front and rear contacts of a-Si solar cells and a conversion efficiency of 12.5 % has been achieved [3]. Furthermore, in order to enhance the uniformity of film thickness and grain size of ZnO films, the atomic layer deposition (ALD) technique was employed [4]. By using the ALD technique, self-limiting growth of ZnO films was achieved and it was found that the films had a good uniformity in thickness, grain size and crystalline structure.

In this study, in order to improve the film quality, the photo atomic layer deposition (photo-ALD) technique was employed for the first time. The effects of ultraviolet (UV) light irradiation during the growth on the structural and electrical properties of the films were examined.

2. EXPERIMENTAL

Fig. 1 shows a schematic diagram of the ZnO deposition system. Diethylzinc (DEZ) and H_2O reactant gases were alternatively fed into the chamber with argon as a carrier gas. The pulse length used were 2 sec for the reactants and 8 sec for the evacuation between the reactants. The pressure in the chamber during deposition was 0.09-0.10 Torr. ZnO films were grown on Corning 7059 glass substrates and the substrate temperature was varied from 105 ℃ to 280 ℃. The UV light was irradiated through the top quartz window of the chamber. A low-pressure mercury lamp was employed as a light source,

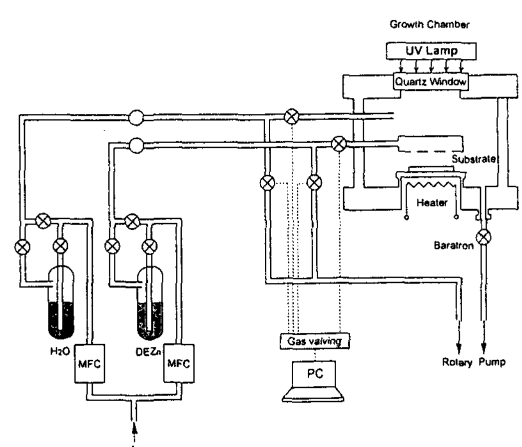

Fig. 1 Schematic diagram of the photo-ALD system.

radiating intense 184.9 nm and 253.7 nm resonance lines.

3. RESULTS AND DISCUSSION

First, the dependence of the deposition rate on the substrate temperature was examined. Fig. 2 shows the deposition rate of ZnO films grown by ALD and photo-ALD techniques as a function of substrate temperature. In the case of ALD technique, the average growth thickness per growth cycle is in good agreement with the ZnO (100) monolayer thickness for the substrate temperature range of 105 to 165 ℃. However, further increase of the substrate temperature results in a non-monolayer growth. In contrast, in the case of photo-ALD technique, the average growth thickness per growth cycle is close to the ZnO (100) or (101) monolayer thickness because of the change of the crystal growth orientation.

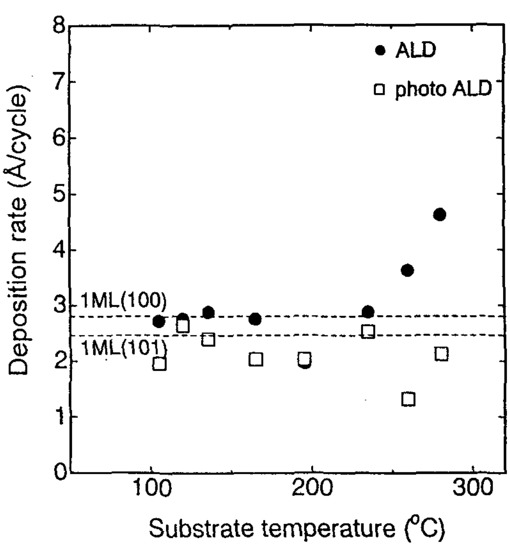

Fig. 2 Deposition rate of ZnO films grown by ALD and photo-ALD techniques as a function of substrate temperature.

Fig. 3 shows the X-ray diffraction spectra of the ZnO film grown by photo-ALD technique at different substrate temperatures. The growth orientations of (100) and (101) are dominant at the low substrate temperatures. By increasing the substrate temperature up to 195 ℃, the peak intensity of (101) and (110) orientations increase, whereas (002) orientation becomes dominant at substrate temperatures higher than 235 ℃. From the study of the film morphology by SEM microscopy, it was revealed that very uniform grain size and crystalline structure were obtained by photo-ALD.

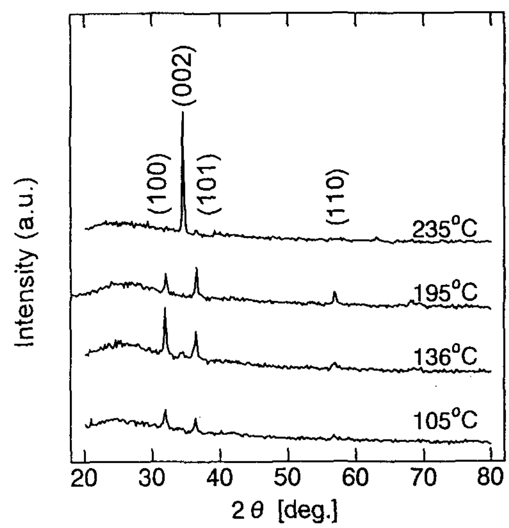

Fig. 3 X-ray diffraction spectra of the ZnO film grown by photo-ALD technique at different substrate temperatures.

The carrier concentrations and electron mobilities were evaluated by the Hall measurement using van der Pauw configuration. Fig. 4 shows the electrical properties of the ZnO films grown by ALD and photo-ALD techniques as a function of substrate temperature. The carrier concentrations of the films grown with UV irradiation are higher than those of the films grown without UV irradiation throughout the entire substrate temperature range from 105 ℃ to 165 ℃. Consequently, the resistivity of the films grown with UV irradiation is one order of magnitude less than that grown without UV irradiation. The minimum resistivity of 6.9×10^{-4} Ω cm was obtained at the substrate temperature of 135 ℃ by photo-ALD method without any

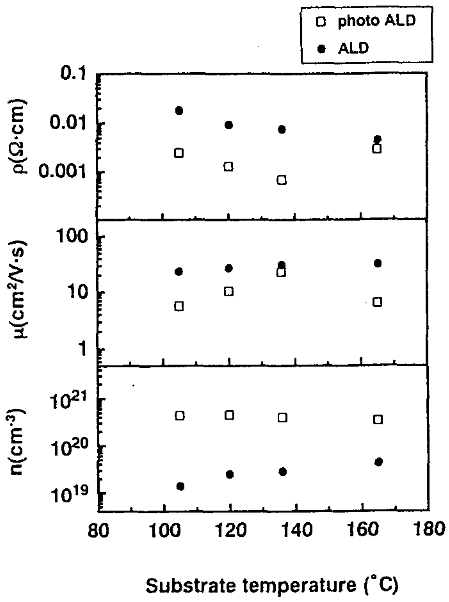

Fig. 4 Electrical properties of the ZnO films grown by ALD and photo-ALD techniques as a function of substrate temperature.

intentional doping. This superior electrical properties of the ZnO films grown by photo-ALD are preferable for application to solar cells.

4. CONCLUSION

A novel photoexcitation process (photo-ALD) was employed to control the ZnO film thickness precisely and improve the film quality. It was found that the UV light irradiation onto the substrate during the growth was very effective in increasing the electron concentration of the ZnO film. The resistivity of the films grown with UV irradiation was one order of magnitude less than that grown without UV irradiation, and the minimum resistivity of 6.9×10^{-4} Ω cm was obtained by photo-ALD method without any intentional doping.

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