

Investigation of solution-processed α -Fe₂O₃ / ZnO multilayer for photoelectrode

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ABSTRACT

α -Fe₂O₃ / ZnO multilayer films fabricated by using spin-spray method and properties of each layer and α -Fe₂O₃ / ZnO film were investigated. First, as-deposited ZnO layer on glass substrate exhibited high transmittance of above 80 % in visible range and a low resistivity. The formation of α -Fe₂O₃ layer on glass substrate was confirmed by XRD. This α -Fe₂O₃ layer was successively deposited on ZnO layer and it was confirmed that α -Fe₂O₃ / ZnO double layered films could be fabricated by aqueous solution process.

1 INTRODUCTION

α -Fe₂O₃ has been studied as a semiconductor usable for gas sensor and semiconductor electrode. Also, it can be applied for environmental purification due to their properties such as water splitting and photodecomposition. Especially in case of water splitting, it can be applied as a photoelectrode to generate hydrogen. Although vacuum process such as sputtering has been used for the deposition method of α -Fe₂O₃ film, they required high deposition temperature. For this reason, solution process is receiving attention as an alternative fabrication method. In this study, we attempted the fabrication of α -Fe₂O₃ / ZnO multilayer film by using spin-spray method. Spin-spray method is one of aqueous solution processes and it has several merits to fabricate functional ceramic films such as high deposition rate and crystallinity without post heating.

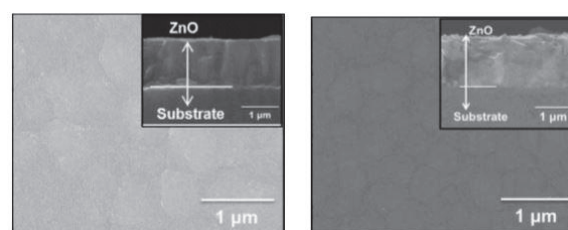
2 EXPERIMENT

ZnO films were deposited on plasma treated glass substrate. The source solution was prepared by dissolving 10 mM Zn(NO₃)₂·6H₂O and the reaction solution was prepared by dissolving NH₃ and 2 and 10 mM Na₃C₆H₅O₇ in same amount of de-ionized water. ZnO films were deposited by spraying these solutions for 10 minutes. And then, as-deposited ZnO films were subjected to UV illumination with BLB lamp to decompose citrate incorporated in the deposited films.

The α -Fe₂O₃ film was deposited for 30 min on glass substrate and as-deposited ZnO films. The source solution of 10 mM FeCl₂·4H₂O and the reaction solution of 20 mM NaNO₂ in de-ionized water were used for the deposition of α -Fe₂O₃ films.

3 RESULTS

Figure 1 shows SEM images of as-deposited ZnO films. All films show dense and smooth surface. Thickness of ZnO films decreased from 1.4 to 1.2 μ m with increasing of citrate concentration from 2 to 10 mM. This result is related to the function of citrate ion to the growth of ZnO crystallites in solutions. As-deposited ZnO film without citrate indicated rod array structure with (002) preferred orientation [1]. However, ZnO film deposited using citrate in solution had continuous structure because citrate ions were absorbed to (001) plane and it suppressed the anisotropic growth along the (001) direction [2]. Since this growth control suppressed the growth speed of ZnO columnar, the thickness was decreased with increasing citrate concentration. Figure 2 shows XRD patterns of ZnO films fabricated by spin-spray method at citrate concentration of 2 mM and 10 mM. The ZnO films are in hexagonal crystallographic phase (JCPDS 36-1451).



(a) Citrate 2 mM

(b) Citrate 10 mM

Fig. 1 SEM images of as-deposited ZnO films

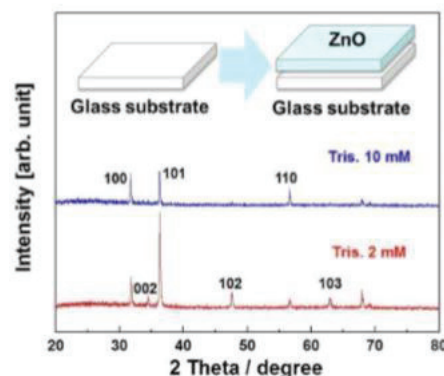


Fig. 2 XRD patterns of as-deposited ZnO films.

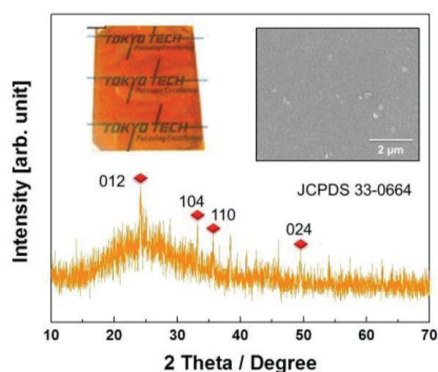
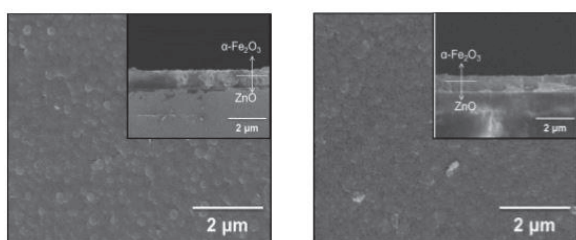


Fig. 3 XRD patterns and SEM images of α -Fe₂O₃ film.



(a) Citrate 2 mM (b) Citrate 10 mM
Fig. 4 SEM images of α -Fe₂O₃ / ZnO multilayer film.

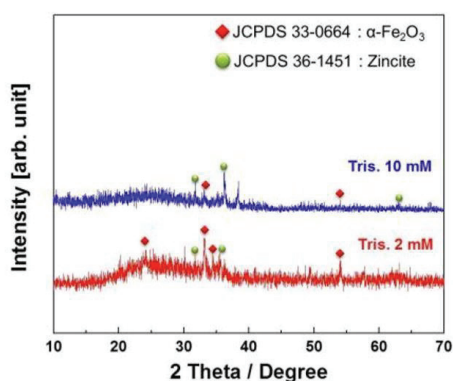


Fig. 5 XRD patterns of α -Fe₂O₃ / ZnO multilayer film.

Figure 3 shows XRD pattern and SEM image of α -Fe₂O₃ film deposited on glass substrate by spin-spray method. All of diffraction peaks were confirmed as α -Fe₂O₃ phase, and other peaks were not found (JCPDS 33-0664). As-deposited α -Fe₂O₃ film had thickness of 320 nm and rough surface. After evaluation of α -Fe₂O₃ film, it was deposited on ZnO films. Figure 4 shows SEM images of as-fabricated α -Fe₂O₃ / ZnO multilayer film deposited at different citrate concentrations during ZnO film deposition. It was confirmed the α -Fe₂O₃ film deposited on as-deposited ZnO films and α -Fe₂O₃ / ZnO multilayer film had indicated dense surface. More details of structural properties were investigated by XRD, as shown in Figure 5. All peaks corresponded to ZnO and α -Fe₂O₃ phase, and no other peaks were found. From the XRD result, we could confirm that the change of structural properties with increasing of citrate concentration. Crystallinities were degraded and thickness of α -Fe₂O₃ / ZnO multilayer was decreased by increasing the citrate concentration.

4 CONCLUSIONS

ZnO and α -Fe₂O₃ films and the α -Fe₂O₃ / ZnO multilayer film were deposited on glass substrate and the structural, crystallographic, and electrical properties were investigated, in this study. As-deposited ZnO films by spin-spray method showed high transmittance above 80 %. α -Fe₂O₃ / ZnO multilayer films were fabricated by deposition of α -Fe₂O₃ layer on ZnO layer. Formation of α -Fe₂O₃ / ZnO multilayer film were verified by XRD, and dense surface properties confirmed by SEM. From these results, we could confirm the successive deposition of ZnO and α -Fe₂O₃ layers are possible by solution method.

REFERENCES

- [1] H. Wagata, N. Ohashi, T. Taniguchi, A. K. Subramani, K. Katsumata, K. Okada, et al., Cryst. Growth Des.10, 3502 (2010).
- [2] H. Wagata, N. Ohashi, T. Taniguchi, A. K. Subramani, K. Katsumata, K. Okada, et al., Cryst. Growth Des.10, 4968 (2010).