ATMOSPHERE DEPENDENCE OF FORMATION PROCESS OF OXYGEN VACANCY IN ZINC OXIDE

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Thermal behavior of 100-ppm Al and ~100-ppt In impurities doped in zinc oxide (ZnO) was investigated under various heat-treatment conditions by means of the time-differential perturbed angular correlation method with the $^{111}In(\rightarrow^{111}Cd)$ probe. Contrasting interactions between Al and ^{111}In impurities were observed depending on the ambient atmosphere to which the samples are exposed; (i) Al and In impurities associate with each other by their thermal diffusion in air, and (ii) the ^{111}In probe is detrapped from the Al aggregations in high-temperature vacuum, resulting in substitution at defect-free Zn sites. Detailed investigation of the thermal behavior of the impurities has revealed that the dissociation reaction is triggered by the formation of oxygen vacancies in the vicinity of the locally-associated In-Al structure. A unique method to determine the activation energy of the oxygen-vacancy formation is presented with the estimated experimental value of $E_a = 0.72(6)$ eV.

I. INTRODUCTION

Defect-induced properties of zinc oxide (ZnO) have been attracting much attention toward their application to functional materials in a wide field of industry. Especially, physical properties brought about by Al ions and/or oxygen vacancies in ZnO are one of the most intriguing topics for the development of future electronic devices. Extrinsic-semiconductor devices such as of Al-doped ZnO are expected to be in use under various ambient conditions; the states of being of impurity ions in the matrix are susceptible to change depending on the condition. For a practical use of Al-doped ZnO device, therefore, we have investigated the local structures in Al-doped ZnO under various ambient conditions by means of the time-differential perturbed angular correlation (TDPAC) method. In one of our previous TDPAC studies, we observed contrasting atmosphere dependence of the stability of aggregations of ^{111}In and Al impurities doped in 100 ppm Al-doped ZnO: (i) Al and In impurities associate with each other by their thermal diffusion in air, and (ii) the ^{111}In probe is detrapped from the Al aggregations in high-temperature vacuum, resulting in substitution at defect-free Zn sites[1,2]. Detailed investigation of the thermal behavior of the impurities has revealed that the dissociation reaction is triggered by the formation of oxygen vacancies. In the present work, in order to extend quantitative discussion on the kinetics of the formation process of oxygen vacancy, we evaluated the formation energy of oxygen vacancy from the temperature dependences of the detrapping process during heat treatment in vacuum[3].

II. EXPERIMENT

For the synthesis of 100 ppm Al-doped ZnO, stoichiometric amounts of $Al(NO_3)_3 \cdot 9H_2O$ and ZnO powder were mixed in ethanol. The suspension was heated to evaporate the ethanol until dryness. The powders were pressed into disks and sintered in air at 1273 K for 3 h. Commercially available ^{111}In HCl solution was added in droplets onto the sintered disks. The initial concentration of ^{111}In ions doped in the sample was typically ~100 ppt. After the disks were dried up by heat, they again underwent heat treatment in air at 1373 K for 2 h. Following the doping of ^{111}In, each disk was separately sealed in different quartz tubes in vacuum, and 24-h isochronal annealing was performed one by one at different temperatures (873~1148 K). The TDPAC measurements were carried out for the 171-245 keV cascade γ rays of the $^{111}Cd(\leftarrow^{111}In)$ probe with the intermediate state of $I = 5/2$ having a half-life of 85.0 ns.

III. Results

It was found from the TDPAC spectra of the ^{111}In(→^{111}Cd) in 100 ppm Al-doped ZnO heat-treated at various temperatures that ^{111}In probes come to detrap from the Al aggregations in high-temperature vacuum by degrees. Detailed investigation of the thermal behavior of the impurities has revealed that this detrapping process is controlled by the first-order rate law. For the first-order reaction of this dissociation process, we obtained the rate constant k at different temperatures. Their temperature variation is plotted in Fig. 1. A least-squares fit to the k values was then carried out with the following Arrhenius equation:

$$k = \nu_0 \exp(-E_a / k_B T) \quad (1)$$

and the activation energy, E_a, was evaluated to be 0.72 (6) eV. Because the dissociation process of the ^{111}In probe and Al would be induced by the formation of oxygen vacancies as discussed above, we suggest that the observed E_a is closely related to the formation energy of oxygen vacancies in Al-doped ZnO sample. This interpretation is supported by the fact that the present E_a value shows good agreement with the theoretical ones calculated for the formation energy of oxygen vacancies in ZnO (0.8 and 1.0 eV)[4,5].

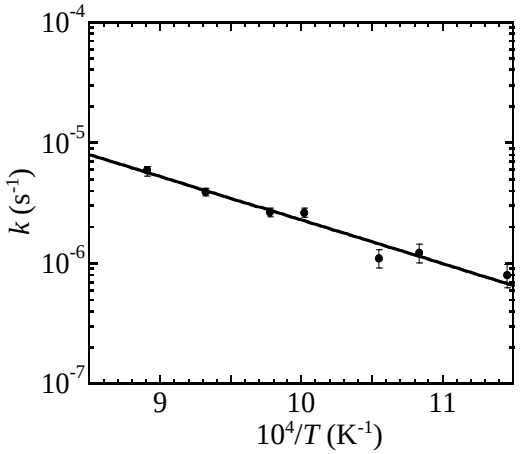

Fig.1. Temperature dependence of the rate constant, k. An Arrhenius equation was used for the fit.

IV. CONCLUSIONS

In the present study, we have investigated the temperature variation of the detrapping process of Al and In ions doped in ZnO heat-treated in vacuum by means of the TDPAC method with the ^{111}In(→^{111}Cd) probe. For quantitative understanding of this detrapping process, we have evaluated the activation energy from the temperature dependences of the dissociation process to be 0.72(6) eV. We suggest that this E_a is related to the formation energy of oxygen vacancies in Al-doped ZnO sample, which is supported by good agreement with theoretical values (0.8 and 1.0 eV). In the session, based on the further investigation of TDPAC spectra for Al-doped ZnO obtained by isothermal annealings in Ar gas atmosphere, we discuss the atmosphere dependence of the formation process of oxygen vacancy.

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