Thermal Behavior of Al and In Impurities Doped in ZnO Studied by Means of Perturbed Angular Correlation Spectroscopy

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Time-differential perturbed angular correlation (TDPAC) measurements with the ^{111}In($\rightarrow ^{111}$Cd) probe were performed for Al-doped ZnO heat-treated under various conditions in order to examine the following dependences on the formation of local structures of Al ions: concentration of Al ions, their diffusion temperature, and ambient atmosphere. Contrasting interactions between Al and ^{111}In impurities were observed depending on the ambient atmosphere to which the samples are exposed; (1) *in air*, Al impurities locally associate with each other to form minute $ZnAl_2O_4$ grains even at extremely dilute concentration of 0.1 ppm, and the ^{111}In($\rightarrow ^{111}$Cd) probe ions of about 100 ppt would be trapped in the field of Al ion(s), but (2) *in vacuum*, the bound state formed in air dissociates by heat treatment, resulting in substitution of ^{111}In ions at defect-free tetrahedral Zn sites. It was also revealed that the dissociation reaction is triggered by the formation of oxygen vacancies in the vicinity of the locally-associated In-Al structures. For a quantitative discussion on the kinetics of the reaction, the annealing-time and annealing-temperature dependences of this dissociation process were investigated. TDPAC experiments have revealed that the relevant dissociation process is controlled by the first-order rate law, and the activation energy E_a for this reaction was evaluated from the temperature dependent rate constants k to be 0.72(6) eV. The proposed dissociation mechanism of the impurities evidently suggests that this E_a corresponds to the formation energy of oxygen vacancies in Al-doped ZnO sample, which is supported by good agreement with theoretical values.

ABSTRACT

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, it is important to study the stability of Al impurities and/or oxygen vacancies under various conditions. The time-differential perturbed angular correlation method (TDPAC) is very suited for that purpose because it can directly provide atomic-level information of impurity atoms.

In this study, TDPAC measurements with the $^{111}\mathrm{In}(\rightarrow{}^{111}\mathrm{Cd})$ probe were performed for Al-doped ZnO heat-treated under various conditions to examine the following dependences on the formation of local structures of Al ions: concentration of Al ions, their diffusion temperature, and ambient atmosphere. It was suggested from the experiments that thermal behaviors of the impurities are closely correlated with the concentration of atmospheric oxygen to which the samples are exposed; (1)

in air, Al impurities locally associate with each other to form minute $ZnAl_2O_4$ grains even at extremely dilute concentration of 0.01 ppm, and the $^{111}In(\rightarrow^{111}Cd)$ probe ions of about 100 ppt are trapped in the field of Al ion(s), but (2) *in vacuum*, the bound state of ^{111}In and Al formed in air dissociates by heat treatment at 1000 K, resulting in substitution of ^{111}In ions at defect-free tetrahedral 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 structures.

In order to extend quantitative discussion on the correlation between the thermal behavior of the impurities and the concentration of atmospheric oxygen, isothermal annealing of ZnO doped with Al and ^{111}In was performed in vacuum. TDPAC experiments have revealed that the relevant dissociation process is controlled by the first-order rate law. In addition, the activation energy E_a for the reaction was successfully evaluated from the temperature variation of the rate constants k to be 0.72(6) eV. The proposed dissociation mechanism of the impurities evidently suggests 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 the corresponding theoretical values (0.85 and 1.0 eV).

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学位論文審査報告書（甲）

１．学位論文題目（外国語の場合は和訳を付けること。）

Thermal Behavior of Al and In Impurities Doped in ZnO Studied by Means of Perturbed Angular Correlation Spectroscopy

和訳：摂動角相関法によるZnOに導入された不純物AlとInの熱的挙動の研究

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３．審査結果の要旨（600～650字）

標記学位論文を各審査委員が個別に審査した後、全委員によって申請者の口頭説明に対する予備審査を実施した。その後、口頭発表会を平成27年2月3日に開催し、発表会終了後、論文審査委員会において論文を審査した。審査結果を以下に記す。酸化亜鉛（ZnO）は不純物の添加によって伝導度が変化するため、不純物の存在状態を把握することは、ZnOの半導体物性を理解する上で重要である。本研究では、^{111}Inをプローブとするγ線摂動角相関法によって試料の熱処理に伴う不純物Alサイトの状態変化を探索した。その結果、1）空気中で加熱した場合、極微量（0.01 ppm）の濃度でもAlは拡散過程において互いに会合して二次相を形成し、この粒界に^{111}Inプローブが強く結合すること、2）真空中でこの結合は解離し、^{111}Inは熱拡散によってZnの格子点を置換することが明らかとなった。申請者は酸素分圧の低下に伴ってこの解離が進行することを実証し、^{111}In近傍の酸素原子の脱離反応が解離を惹起するという仮説を立てた。さらにこの解離反応を定量的に理解するため、^{111}Inの状態変化の焼成時間依存性を各温度で調べた結果、反応が一次の速度則に従うことが判明し、速度定数の温度依存性から反応の活性化エネルギー（E_a = 0.72(6) eV）を求めることに成功した。理論計算との照合により、この値がZnOの酸素空孔形成エネルギーに相当することを示した。

本研究成果はZnO中での不純物Alの存在状態ならびに状態変化を明確に捉えたもので、ZnOの半導体物性の理解と制御に資するものである。従って、本博士論文は博士（理学）の学位に値すると判断した。

４．審査結果　(1) 判　　定（いずれかに○印）　（合　格）・　不合格

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