

Redox Reaction of Defect Species in ZnO Modified with Cu²⁺

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The ZnO modified with Cu²⁺ were prepared and characterized by ESR. The novel redox reaction in ZnO bulk was observed from the time course of ESR signal intensities of defect species and Cu²⁺ in the Cu²⁺-modified ZnO.

Zinc oxide(ZnO) and its modified ones are widely used as the advanced materials such as catalysts, sensors, photoconductor devices, voltage variable resistors and so on. These applications originate from the ZnO exhibiting the characteristics of n-type semiconductor, and being further extended by the development of characterization methods. We call the attention to an ESR method for the advanced inorganic materials, and have applied to ZnO in this study.

Though a normal oxidation state of zinc ion(Zn²⁺) is inactive for ESR, ZnO is an n-type semiconductor to give rise to ESR signal for Zn⁺ and color center(unpaired electron trapped in oxygen vacancy, Fs⁺) in addition to adsorbed oxygen species

with unpaired electron.¹⁻³ The former species give an ESR signal around g=1.96, and is considered to play an important role in the properties of ZnO. We report novel behaviors for redox reaction taking place in ZnO bulk.

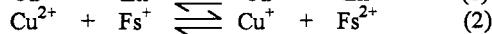
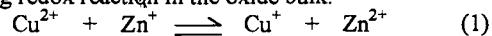
Chemicals used were reagent grade without active impurities for ESR. An aqueous solution of sodium carbonate was added to an aqueous solution of zinc nitrate and a metal nitrate. The coprecipitate of zinc and metal ion hydroxycarbonate was obtained and it was calcined at 873 K in air to prepare the ZnO modified with metal ion(Mⁿ⁺-modified ZnO, Mⁿ⁺ : Al³⁺, Mg²⁺, and Cu²⁺).⁴ The oxides thus obtained was identified as a single phase of ZnO by XRD measurements (Shimazu, XD-D1). ESR spectra were recorded with a JEOL JES-FR30 spectrometer operating X band mode at 77 K. The powdery oxide(50 mg) of powdery oxide was loaded in a quartz tube closed with a plastic cap in air, and was subjected for the measurement of ESR spectra. The g values were calibrated by Mn²⁺ in MgO as a standard, and the signal intensity was normalized by the same standard.

As shown in Figure 1, an ESR signal of ZnO at g=1.96 (Figure 1a) may be assigned to that of Zn⁺ and Fs⁺, and gives slight unsymmetrical shape for base line because of two signal with very similar g values(Figure 1a). The modification with Al³⁺ causes an increase in the signal intensity(Figure 1b). The divalent ions of Zn²⁺ are substituted with Al³⁺ to increase the formation of defect species such as Zn⁺ and Fs⁺ by charge compensation. The Mg²⁺ as modification ion decreases the signal intensity to depress the formation of defect species(Figure 1c).

The Cu²⁺-modified ZnO decreased the signal intensity at g=1.96(Figure 1d). When an atomic ratio of Cu/Zn was increased, this signal disappeared(Figure 1e). The signal at lower magnetic field(g=2.05) is due to paramagnetic Cu²⁺, and the intensity was increased with atomic ratio of Cu/Zn.

There was no effect of time-course on the signal intensity at g=1.96 in the Al³⁺ and Mg²⁺-modified ZnO. The signal intensity of Cu²⁺-modified ZnO varied with time by standing in desiccator at room temperature as shown in Figure. 2 measured for the ZnO with Cu/Zn=0.001. When ESR spectrum was measured immediately after the preparation by calcining the hydroxycarbonate precursor at 873 K, the signals of defects and Cu²⁺ were slightly observed(Figure 2a). The both signal intensities were increased with time on standing(Figure 2b). The oxide with the signal of Figure 2b was heated at 873 K in air to result in the decrease in the signal intensity(Figure 2c). When this oxide was allowed to stand once again, the signal intensity was restored and increased with time(Figure 2d).

These behaviors of ZnO may be explained on the basis of the following redox reaction in the oxide bulk.



Where Fs²⁺ means oxygen vacancies, which is inactive for ESR. The equilibrium lies so far to the right to result in a decrease in ESR signal intensity after the thermal treatment of

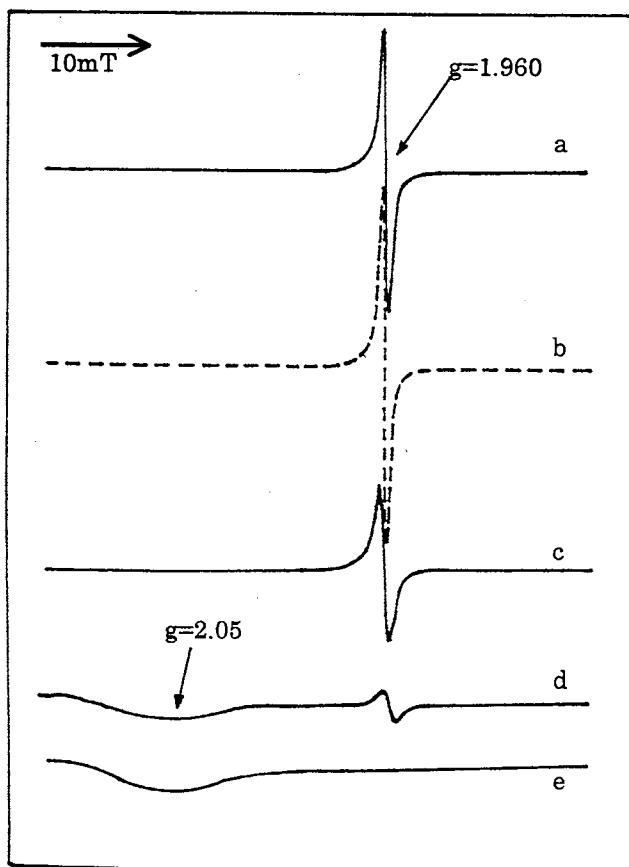


Figure 1. ESR spectra of ZnO modified with various metal ions at 77 K; (a) ZnO, (b) Al³⁺- modified ZnO (Al/Zn=0.02), (c) Mg²⁺- modified ZnO(Mg/Zn=0.02), (d) Cu²⁺- modified ZnO(Cu/Zn=0.002), (e) Cu²⁺- modified ZnO(Cu/Zn=0.001).

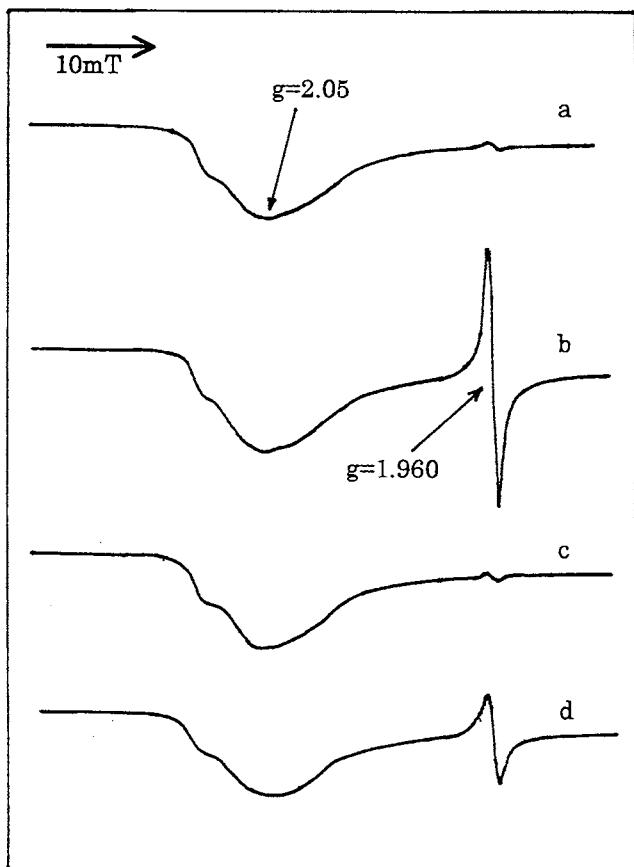


Figure 2. Time course of ESR spectra of Cu^{2+} -modified $\text{ZnO}(\text{Cu}/\text{Zn}=0.001)$ at 77 K; (a) after preparation at 873 K, (b) after 48 days, (c) after heating the sample b at 873 K, (d) after standing the sample c for 48 days.

oxide, and the reverse reaction toward to the left proceeds slowly to regenerate ESR active species at room temperature. The ZnO modified with CuO is an active catalyst for the hydrogenation of CO to CH_3OH .^{5,6} It has been suggested that Cu^+ is one of active species by XPS and EXAFS.⁷⁻⁹ This modification of ZnO causes the reduction of Cu^{2+} to Cu^+ by Zn^+ during the preparation of oxide at 873 K. It seems reasonable to assume the reaction(1). The reaction(2) shows that the electron trapped in Fs^+ gives donor level to act as reducing agent for Cu^{2+} at higher temperature. Since ZnO with a band gap energy of 3.2 eV becomes yellow during thermal treatment, Fs^+ as the electron donor is presumed to be weak reducing agent for Cu^{2+} . The reactions on standing the oxides at room temperature result in the regeneration of ESR active defect species.

The ESR signal intensity or the area of the signal corresponds to the concentration of ESR active species. Figure 3 shows the time courses of the signal height at $g=1.96$ and the area of signal at $g=2.05$. The synchronous increase and decrease

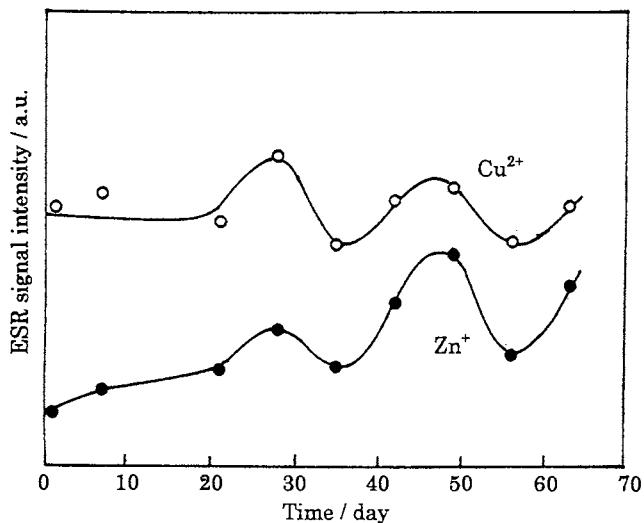


Figure 3. Time course of ESR signal intensity of Cu^{2+} and Zn^+ in Cu^{2+} -modified $\text{ZnO}(\text{Cu}/\text{Zn}=0.001)$.

in the concentrations of both ESR active species are periodically repeated. The reactions(1) and (2) are not thermodynamically in equilibrium at room temperature, and oscillating reaction is presumed in non-equilibrium.

When the oscillating reaction is assumed, the participation of additional reactants must be taken account. Active oxygen species such as O_2^{2-} and O^- would be supposed to be involved in this reaction system. These are active for ESR and give g value around at 2.0. Since this g value is close to that of Cu^{2+} , it is difficult to detect oxygen species in ESR of the Cu^{2+} -modified ZnO . The further study is needed by using the ZnO modified with other metal ions.

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