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Electron Spin Resonance of Oxidized ZnO at -195°C

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An asymmetric ESR spectrum of ZnO at the g value of 1.96 was found to split into $g=1.957$ and 1.963 components at -195°C provided that ZnO was pretreated with oxygen. Temperature dependence of these two signals as well as the effect of doping Al^{3+} or Li^+ on their intensities were investigated to qualify these signals. It was suggested that the $g=1.957$ signal is correlated with conduction electrons while the $g=1.963$ signal is ascribable to electrons trapped at interstitial zinc ions. The ZnO sample also gave rise to another signal at $g=2.013$ at -195°C. The signal was attributed to holes in the bulk.

As has been recognized by numerous workers, a highly outgassed ZnO sample produces a broad and asymmetric ESR spectrum around the g value of 1.96 at room temperature.[1] While this signal has been interpreted as due to electrons in the bulk, some detailed arguments were previously made concerning the origin of the electrons.[2] Recently, Codell *et al.*[3] reported that the signal splits into two components ($g=1.961$ and 1.965), when ZnO is pretreated with tertiary butyl hydroperoxide vapors and subjected to ESR mesurements at -195°C. During the course of our work,[4] we have also recognized that the $g\sim1.96$ signal is replaced by a doublet at -195°C in accordance with the report of Codell *et al.* with respect to a ZnO sample pretreated with O_2. A similar phenomenon was reported more recently by Iyengar *et al.*[5] who pretreated ZnO with N_2O, NO or Cl_2 at 25°C.

In view of these results, it was felt necessary to further investigate the nature of the two component signals and to elucidate the relationship between the $g\sim1.96$ signal and the two components. Since doping of ZnO with Al^{3+} or Li^+ is expected to control the concentration of electrons or interstitial zinc in the bulk, it should be interesting to investigate ESR spectra of the doped ZnO samples and to see how the $g\sim1.96$ signal is modified at -195°C. On the other hand, we have already noted that another signal appears at $g=2.013$ which is distinguishable from that due to adsorbed O_2^- ($g=2.002$, 2.008, 2.051)[4] when an oxidized ZnO is subjected to ESR measurement at -195°C. Undoubtedly, there still remains a question of interest on the ESR spectra of ZnO especially at low temperatures. In the present paper the results of such ESR investigations are reported using Al^{3+} or Li^+ doped ZnO and undoped one, respectively.

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Experimental

ZnO of high purity (Pb: 0.003%, Fe: 0.0001%, other metal: 0.01%) supplied by Sakai Chemical Co., was used for experiments. ZnO samples doped with Al^{3+} or Li^+ were prepared as follows. A powdered ZnO was slurried with dilute aqueous solution of $Al(NO_3)_3 \cdot 9H_2O$ (Guaranteed, Kanto Chemical Co.) and $LiNO_3$ (Guaranteed, Koso Chemical Co.) respectively and dried at 100°C. It was then calcined in air at 500°C for two hours and at 700°C for another hour. The degree of doping was so adjusted that 1.5 mol percent Li_2O or Al_2O_3 is incorporated. Li_2CO_3 was also used instead of $LiNO_3$ to investigate the effect of anion. No difference was found, however, between the two anions.

ESR measurements were made at room temperature and −195°C respectively using a JEOL-P-10 type spectrometer (X-band, 100 kcps field modulation). ZnO samples were placed in a quartz tube (4 cm long, 4 mm id), at the center of which a sealed capillary containing $MgO : Mn^{2+}$ was inserted as a means of measuring relative ESR sensitivity. The spin concentrations of ESR signals were determined by the first moment of the derivative absorption curve, normalized with the intensity of Mn^{2+} signal which was calibrated at room temperature and −195°C with a solution of DPPH (5×10^{-5}M) in benzene substituted for the ZnO sample.

Results and Discussion

Pretreatment of vacuum outgassed ZnO with a small amount of oxygen at room temperature usually results in a decrease in the ESR spectral intensity of the $g \sim 1.96$ signal without perceptible change in its signal shape.[4] Such a spectrum observed at room temperature is illustrated in Fig. 1-a. It was found, however, that the signal is replaced by two *components* ($g = 1.963 \pm 0.001$ and 1.957 ± 0.001) as shown in Fig. 1-b when measured at −195°C. Further pretreatment of the ZnO with 30 Torr O_2 at 200°C for 30 min, followed by evacuation at room temperature, gave a spectrum of Fig. 1-c at −195°C. It is apparent from Figs. 1-b and 1-c that the spin concentrations of the $g = 1.963$ component markedly decrease with the oxygen pretreatment or oxidation of the ZnO sample, while the $g = 1.957$ signal remains nearly constant.

We shall start with a raw ZnO sample (no pretreatment) and investigate how the spin concentrations of the two signals vary with successive oxygen pretreatments of the sample. The untreated ZnO sample showed only the $g = 1.957$ signal when measured at −195°C in a vacuum (stage 1) which we have called so far the $g \sim 1.96$ signal. The ZnO sample was then outgassed at 500°C in a high vacuum for 30 min and then allowed to contact with 30 Torr O_2 at room temperature. The sample was then evacuated for residual oxygen at room temperature and subjected to ESR measurements at −195°C (stage 2). It was found that the original $g = 1.957$ signal is accompanied by the $g = 1.963$

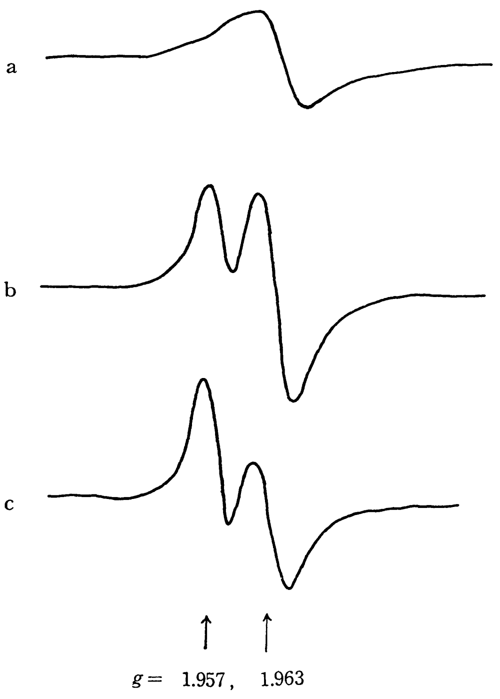

Fig. 1. ESR spectra of ZnO pretreated with oxygen measured at room temperature (a) and −195°C (b, c).

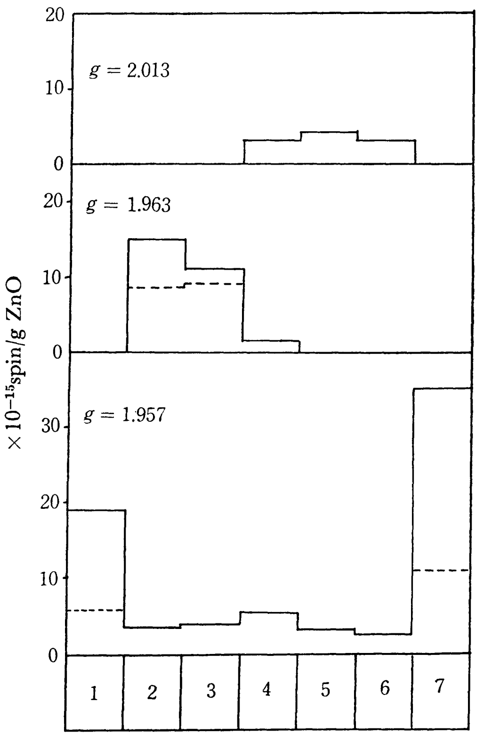

Fig. 2. Effect of successive pretreatments of ZnO on ESR signals. Dashed line indicates spin concentrations at room temperature.

signal; the $g \sim 1.96$ signal was now replaced by the $g=1.957$ and 1.963 signals as already shown in Fig. 1-b.

Changes in the spin concentrations of the two signals were further investigated by treating the ZnO sample at higher temperatures under 30 Torr oxygen (200, 350 and 500°C for stage 3, 4 and 5 respectively). It was found in this way that the $g=1.963$ signal entirely disappears by heat treatment above 350°C whereas the $g=1.957$ remains quite stable up to 500°C. The ZnO sample at stage 5 was kept at room temperature for 5 days (stage 6) where little change was observed in signal intensity. The growth or decay of the two signals with heat treatment in ambient oxygen is illustrated in Fig. 2, where annexed figures 1—6 indicate successive stages for pretreatment. It is apparent from Fig. 2 that the $g=1.957$ and 1.963 species are energetically different.

In stage 7, the ZnO sample was allowed to contact with water vapor. As a result, the 1.957 signal increased to a remarkable extent while the 1.963 signal remained unaffected. As the electric conductivity of ZnO increases on adsorbing water vapor⁶⁾ and dereases on adsorbing oxygen, the growth or decay of the 1.957 signal, as demonstrated in Fig. 2, should be correlated with the change of the concentration of conduction electrons in the bulk of ZnO.

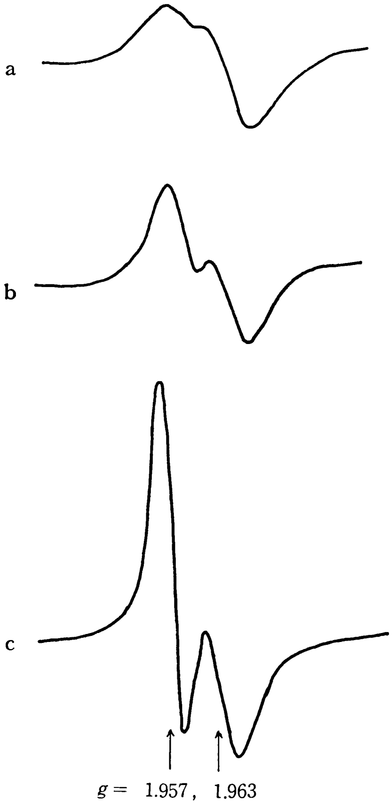

Fig. 3. ESR spectra of ZnO pretreated with oxygen measured at −100°C (a), −150°C (b) and −195°C (c).

Figure 3 indicates the temperature dependence of the $g=1.957$ and $g=1.963$ signals for the ZnO pretreated with 30 Torr O_2 at 200°C for 30 min. ESR measurements were carried out at −100°C (a), −150°C (b) and −195°C (c) respectively. According to Fig. 3, the $g=1.957$ species seems to be more temperature dependent than the $g=1.963$ species. This suggests that the $g=1.957$ species is originated from lower energy levels.

It is generally accepted⁷⁾ that Al^{3+} doped ZnO contains more electrons than an undoped one:

$$\text{ZnO crystal} + Al_2O_3 \rightleftarrows 2Al^{3+} + 2\ominus + 2ZnO + 1/2O_2$$

Conversely, Li^+ doped ZnO contains less electrons:

$$\text{ZnO crystal} + LiO_2 \rightleftarrows 2Li^+ - 2\ominus + 2ZnO - 1/2O_2$$

Attempts were made, therefore, to investigate the behavior of the $g=1.957$ signal with Al^{3+} and Li^+ doped ZnO samples respectively. The doped ZnO samples with or without oxygen pretreatment were subjected to ESR measurements at −195°C. It was found, as shown in Table 1, that the $g=1.957$ signal increases with Al^{3+} doped ZnO while it vanishes completely with Li^+ doped ZnO irrespective of pretreatment. The result is qualitatively in accord with the above equations, *viz*, the $g=1.957$ signal could be attributable to electrons whose behavior is largely in parallel with that of conduction electrons.

Table 1. Spin concentrations ($\times 10^{-15}$ spin/g) of the $g=1.957$ and 2.013 signals

Sample	Pretreatment	$g=1.957$	$g=2.013$
Al-ZnO	A	270	0
	B	120	0
Li-ZnO	A	0	7
	B	0	6

A: Sample evacuated at room temperature.
B: Sample heated at 500°C under 100 Torr of oxygen for 30 min.

Generally speaking, ZnO may contain cation and anion vacancies and many other defects which act as acceptors or donors. Electrons in the bulk of ZnO are expected to be either in the conduction band or localized in donor states, *e.g.*, interstitial Zn_i^+ ion, or trapped at oxygen ion vacancies. Oxygen ion vacancies are considered to be stable

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below the Tamman temperature of ZnO[8] (900°C) and may capture electrons produced upon Al^{3+} doping. Thus the electrons trapped at the oxygen ion vacancies could also contribute to the signal $g=1.957$. Interstitial Zn_i^+ ions are known[9] to be rather labile and may disappear completely upon heating at 550°C for a few minutes in air. It appears, therefore, that electrons responsible for $g=1.957$ may not correspond to the interstitial zinc ions. The thermal behaviour of the $g=1.963$ signal, on the other hand, seems to be consistent with that of Zn_i^+ ions; electrons responsible for the $g=1.963$ signal could be localized at these defects. However, another possibility that the $g=1.963$ signal is due to electrons trapped at the oxygen vacancies near surface[8] may not be excluded. The trapping site near the surface would be distorted to a greater extent as compared with that in the bulk, leading to a slight shift in their g values.

During the course of the above measurements the ESR spectra were accompanied with another signal at the g value of 2.013 ± 0.001. The signal does not seem to be due to contaminated impurities such as Fe^{3+} in ZnO[10] ($g=2.0056$, 2.0041) but due to intrinsic defects in ZnO. In Fig. 2, changes in the spin densities of the 2.013 signal in the successive stages were also illustrated. As shown in stage 7, the $g=2.013$ signal completely disappeared when water vapor was adsorbed on ZnO. It should be noted that the direction of change is opposite to that of the $g=1.957$ signal. This fact may suggest that the $g=2.013$ signal originates from holes in acceptor levels. The supposition is consistent with the experimental result obtained with doped ZnO samples; as shown in Table 1, Li^+ doped ZnO, that is expected to contain *holes*, definitely gave rise to the $g=2.013$ signal while it was absent with Al^{3+} doped ZnO. The $g=2.013$ signal showed no dipolar broadening at high pressures of oxygen, suggesting that it is a bulk species. It would be interesting to investigate whether or not the $g=2.013$ species are correlated with the zinc ion vacancies as suggested by Matsushita and Nakata[11] from their studies on the infrared absorption spectroscopy of a ZnO sample.

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