A Study on Thermoluminescence of Zinc Oxide

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Zinc Oxide 의 Thermoluminescence 에 대한 연구

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초   록

Zn 산화물은 산외 증기 그리고 헬륨 각자의 분위기에서 열커리 한후 그 각자에 대한 열광성을 83°~300°K 의 온도 범위에서 연구하였다. Zn 산화물의 열광성은 900°C 이상의 온도에서는 산소의 부분압에 의존하며 그 최대 강도는 1/T 에 비례하였다. 이 성질을 유발한다고 믿어지고 있는 비희학양론적인 결함의 주 요인은 2개의 전자를 trap 하는 산소 이온의 vacancy 라고 믿어지고 있다. Trap 된 전자의 활성화에너지는 0.13ev 있다.

1. INTRODUCTION

Thermoluminescence studies have been made with various metal oxides such as thoria[1] and alpha niobium pentoxide[2]. This phenomenon, moreover, has been shown to be related to the excitation of electrons from discrete traps such as negative ion vacancies [3~5]. Thermoluminescence is observed by heating a sample at a constant rate and recording the intensity of the light emitted as a function of temperature. Peaks in the glow curve characterize the existence of discrete electron traps.

A model which can explain thermoluminescence in the sulfides has been given by Lambe and Klick[6]. According to Grossweiner[7], the energy depth of a trap for a first-order decay is

$$E = 1.51 kT' T''/(T' - T'') \tag{1}$$

where T'' = the absolute temperature at a glow peak maximum.

T' = the absolute temperature at which the low-temperature side of the glow peak attains one-half of its maximum intensity.

Using Equation (1) and the experimental values of the glow curve peaks obtained, the activation energies, E are evaluated.

Many investigators [1~5] have suggested that thermoluminescence in ionic crystals may be associated with the liberation of electrons from F-centers. Greener, Hirthe and Angino[1] studied the thermoluminescence of thoria in the temperature range 300°K~600°K, and found a large symmetrical glow peak in unirradiated thoria at 468±5°K. Upon irradiation with Co60 gamma radiation, a smaller peak was observed at 338±5°K. The Peak at 468°K corresponds to a first-order decay reaction and the one at 338°K may be the result of a second-order decay. The calculated activation ener-

gies are 1.22 ± 0.05ev for the 468°K peak and 0.65 ± 0.10ev for the 338°K peak. Greener, Fehr and Angino[2] studied the thermoluminescence of alpha niobium pentoxide in the temperature range 300°K~600°K and found two peaks at 513°K and 383°K corresponding to a model of an oxygen vacancy with two trapped electrons.

It is our purpose to investigate the thermoluminescent behavior of zinc oxide in the temperature range 83°K~300°K, and to explain the thermoluminescent behavior of zinc oxide material on the basis of current knowledge of defect structures in zinc oxide.

2. EXPERIMENTAL PROCEDURE

2-1 Specimen Preparation

High purity powdered zinc oxide was obtained from the Mallinckrodt Chemical works in U.S.A., The maximum limits of impurities in the specimens are as follows.

Arsenic	—	0.0002%
Chloride	—	0.001%
Insoluble in H_2SO_4	—	0.010%
Iron	—	0.001%
Lead	—	0.-05%
Manganese	—	0.0005%
Sulfates	—	0.10%
Sulfur Compounds	—	0.010%

The high purity powder was heated in a platinum wound furnace to various temperature in an atmosphere of oxygen, air or helium held at the temperature for 40 minutes, and then slowly cooled to room temperature at a rate of about 100°C/hr in order to produce different concentration of nonstoichiometric point defects.

From basic thermodynamic considerations, the concentration of non-stoichiometric defects is proportional to the oxygen partial pressure according to the relationship

$$n = kPo_2^{-1/t}$$

where n is the concentration of defects, P_{o_2} is the oxygen partial presure, and K is the temperature dependent equilibrium constant. All of the specimens and their annealing treatments prior to the thermoluminescence investigations are summarized in Table I.

2-2 Experimental Apparatus

A block diagram of the apparatus is shown in Figure 1. The diameter of the brass vacuum canister(A) is 2 1/2inches and its length is 10 inches. It contains a heating unit (B) which consists of a strip of lavite 1 1/2 inches×1 1/2 inches×1/5 inch wound five times with No. 28 chromel wire. This heater is capable of heating the specimen from the temperature of liquid nitrogen to about 300°K. A quartz light pipe (C) 1 3/8 inches in diameter and 4 inches long is centered in the canister and serves to conduct the emitted light to the quartz window(D). Thelight is transmitted through the window to a photomultiplier sensing unit (O) manufactured by the Photovolt Corporation (Model 520-M). The canister is immersed in a Dewar flask (M) filled with liquid nitrogen to cool the spe-
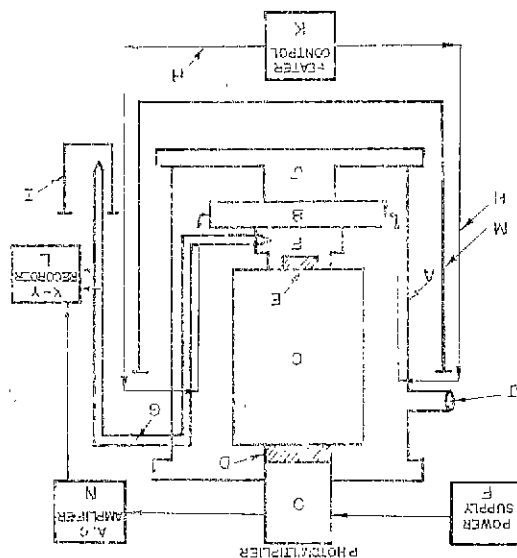

Fig 1. Block diagram of apparatus
A······Brass Vacuum Canister
B······Heating Unit
C······Quartz Pipe
D······Quartz Window
E······Sample
F······Silver Sample Holder
G······Thermocouple
H······Heater Leads
I······Ice for Standard Reference
J······Connection for Vacuum Tube
M······Silver Dewar Flask

Table 1 Description of specimens

Specimen Number	Material	Annealing Temperature(°C)	Annealing Time(Min.)	Annealing Atmosphere
1	ZnO	As Received		
2	ZnO	200	40	Air
3	ZnO	500–520	40	Oxygen
4	ZnO	600–620	40	Oxygen
5	ZnO	740–760	40	Oxygen
6	ZnO	875–900	40	Oxygen
7	ZnO	900	40	Air
8	ZnO	900	40	Helium
9	ZnO	975	40	Oxygen
10	ZnO	1000	40	Air
11	ZnO	1100	40	Oxygen
12	ZnO	1100	40	Air
13	ZnO	1200	40	Oxygen
14	ZnO	1300	40	Oxygen

cimen to 83°K before the start of the run. The specimen holder (F) is a silver disc about 5/8 inches in diameter and 1/16 inches thick. A chromel-alumel thermocouple (G) is soldered into a hole in the holder to measure the temperature The output of the photomultiplier is the signal for the Y-input of an Electro Instruments (Model 100) X-Y recorder (L) and the X-input is provided by the thermocouple. The graph of intensity versus temperature is the well -known glow curve as shown in Figure 2 for ZnO annealed in oxygen at 975°C for 40 minutes and than irradiated with ultraviolet radiation for 45 minutes at 83°K.

2-3 Experimental Technique

The powder specimen is placed in the cavity of the specimen holder at room temperature. The system is then evacuated to a pressure of about 1mm. mercury and cooled to the temperature of liquid nitrogen. The time to the liquid nitrogen temperature is recorded and the specimen is irradiated with ultraviolet radiation from a commercially available "Mineralite" for a pressure of about 1mm. mercury and cooled to the temperature of liquid nitrogen. The time to cool to the liquid nitrogen temperature is recorded and the specimen is irradiated with ultraviolet radiation from a commercially available "Mineralite" for a preselected length of time. After exposure is complete, the spe-
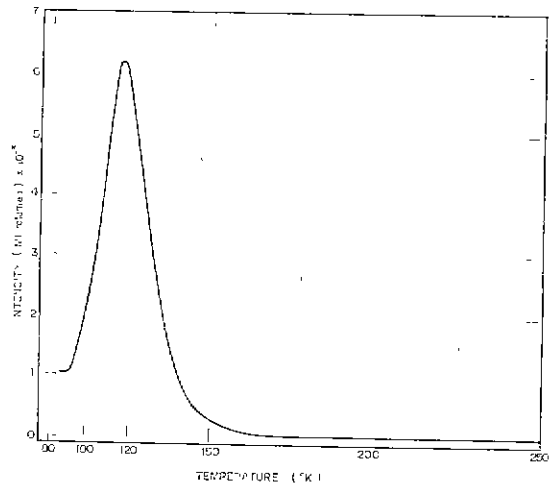

Fig. 2. A typical glowcurve for ZnO with irradiated U. V. 45min. (RUN #9B)

cimen is heated at a constant rate of 2° per 3 seconds by means of Honeywell programmed controller from 83°K to about 300°K.

During the heating process, the light intensity is measured using the photomultiplier tube and the current from the tube is amplified to a convenient level for recording on the X-Y plotter. The X-Y recorder graphs the emitted light intensity as a function of the specimen temperature to give the characteristic glow curve.

3. RESULTS AND DISCUSSION

The thermoluminescence of zinc oxide was studied using the above described technique and the results are summarized in Table II and the glow curves shown in Figures 4-12. All of the curves exhibit a single peak whose position (temperature), magnitude (intensity), and shape are a function of the prior annealing treatment or the weight of the specimen employed.

Table II. Summary of data for zinc oxide

Specimen No.	Run No.	Anneal. Temp. (°C)	Anneal. Time (Min.)	Anneal. Atmos.	Specimen Wt. (mg.)	U. V. Time (Min.)	Max. Intensity (Microlumen $\times 10^3$)	Peak Temp. (°K)	Temp. at $I_{max}/2$ (°K)
1	1				300	15	2.99	108	103
1	1A				300	30	1.84	99	95
1	1B				300	45	1.60	110	98
2	2	200	40	Air	300	15	3.16	110	97
2	2A	200	40	Air	300	30	4.18	110	94
2	2B	200	40	Air	300	45	2.56	113	102
3	3	500-520	40	O_2	300	45	1.49	111	103
4	4	600-620	40	O_2	300	45	1.32	105	955
5	5	740-760	40	O_2	300	45	1.61	111	102
6	6	875-900	40	O_2	300	45	1.50	118	102
7	7	900	40	Air	300	45	12.80	118	100
8	8	900	40	He	300	45	23.50	115	105
9	9	975	40	O_2	300	15	4.14	128	107
9	9A	975	40	O_2	300	30	4.63	121	103
9	9B	975	40	O_2	300	45	6.22	117	105
10	10	1000	40	Air	300	45	26.70	115	104
9	9C	975	40	O_2	300	60	5.17	119	107
9	9D	975	40	O_2	300	120	5.54	118	106
11	11	1100	40	O_2	300	45	21.00	122	103
12	12	1100	40	Air	300	45	66.70	120	111
13	13	1200	40	O_2	300	30	25.20	118	100
13	13A	1200	40	O_2	300	45	84.50	116	98
13	13B	1200	40	O_2	1000	60	28.50	145	130
14	14	1300	40	O_2	300	15	25.30	124	105
14	14A	1300	40	O_2	300	45	56.33	119	111

The first series of experiments was run to determine the dependence of thermoluminescence on the length of exposure to ultraviolet radiation. It can be seen from Figures 4-5 that for exposure times of 30 minutes or less, the specimens annealed in air at 200 °C for 40minutes and those in the as received condi-

tion exhibit non-symmetrical peaks in their respective glow curves.

A suggested dexplanation for these observations may be the existence of a small concentration of impurity levels below the intrinsic defect levels found in the oxide. (See Figure 3) with small amounts of irradia-
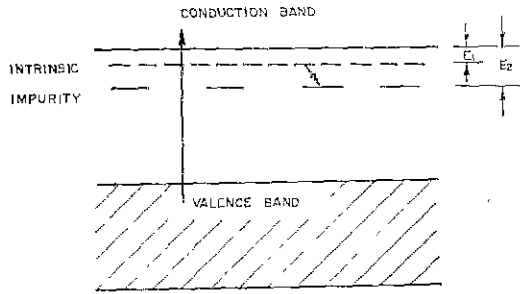
Fig. 3 A model to explain the existence of a nonsymmetrical peak in ZnO for short irradition times.
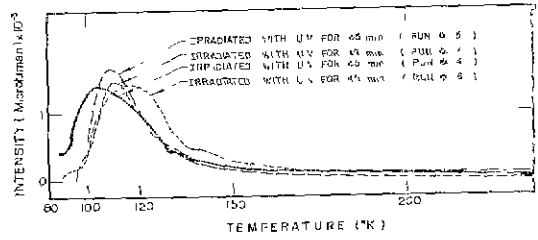

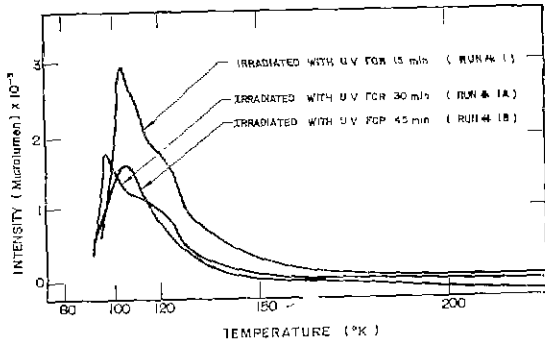Fig. 6. Glow curve of ZnO irradiated with U. V. for 45 min. (RUN #3, 4, 5 and 6)

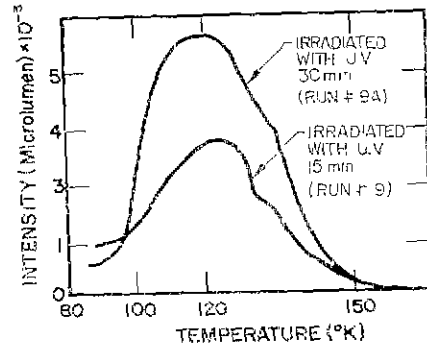Fig. 4. Glow curve of ZnO irradiated with U. V. for 15, 30 and 45min. (RUN #1, 1A AND 1B)

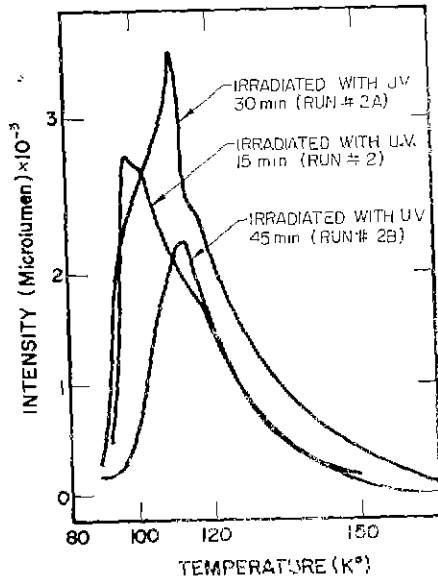Fig. 7. Glow curve of ZnO irradiated with U. V. for 15 min. and 30 min. (RUN #9 and 9A)

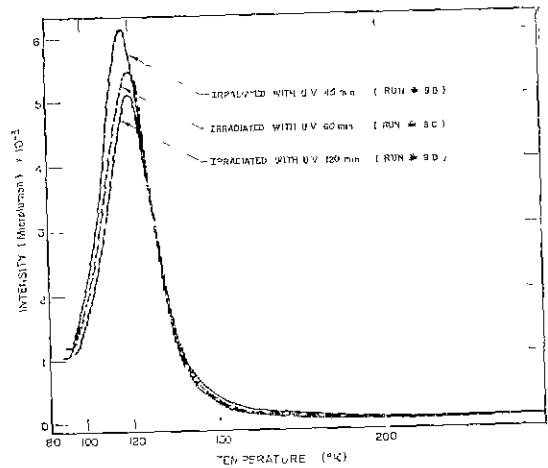Fig. 5 Glow curve of ZnO irradiated with U. V. for 15, 30, and 45 min. (RUN #2, 2A and 2B)

Fig. 8. Glow curve of ZnO irradiated with U. V. for 45, 60, and 120 min. (RUN #9B, 9C and 9D)
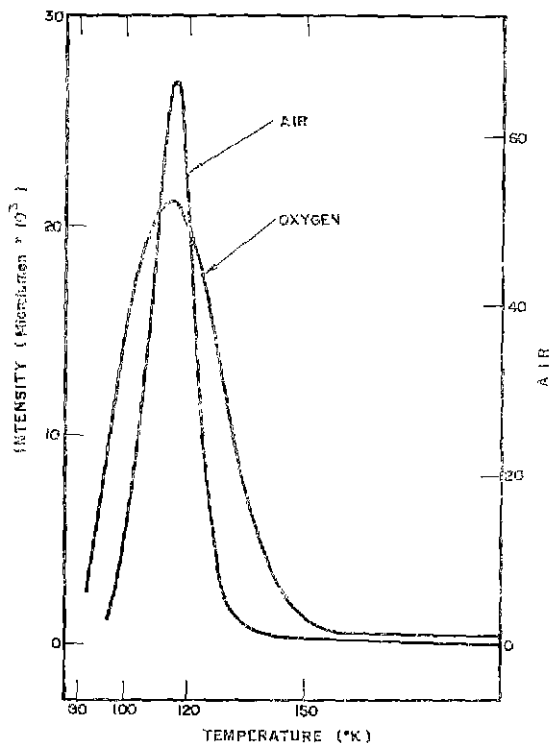
Fig. 9. Glow curvers for ZnO annealed in oxygen and air at 1100°C for 40 minutes and irradiated with U. V. for 45 minutes. (RUN 11 and 12)
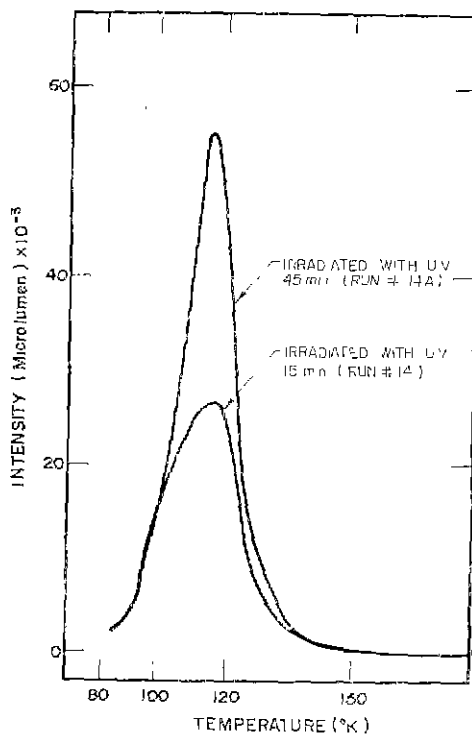

Fig. 11. Glow curve of ZnO irradiated with U. V. for 15 and 45 min. (RUN #14 and 14A)
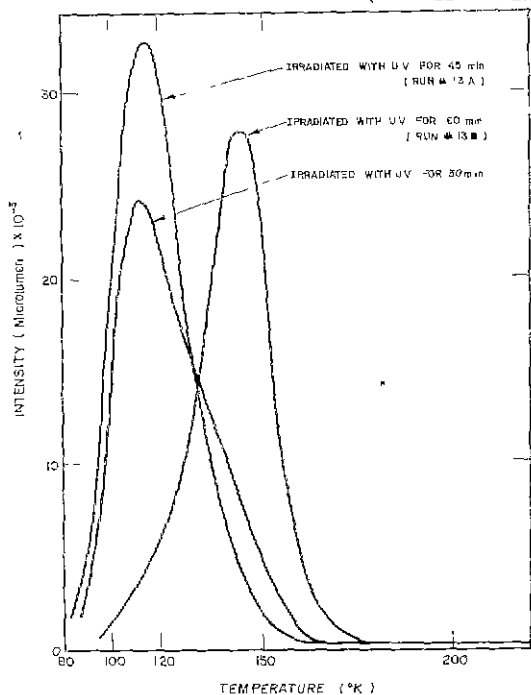

Fig. 10. Glow curve of ZnO irradiated with U. V. for 30, 45, and 60min. (RUN#13, 13A and 13B)
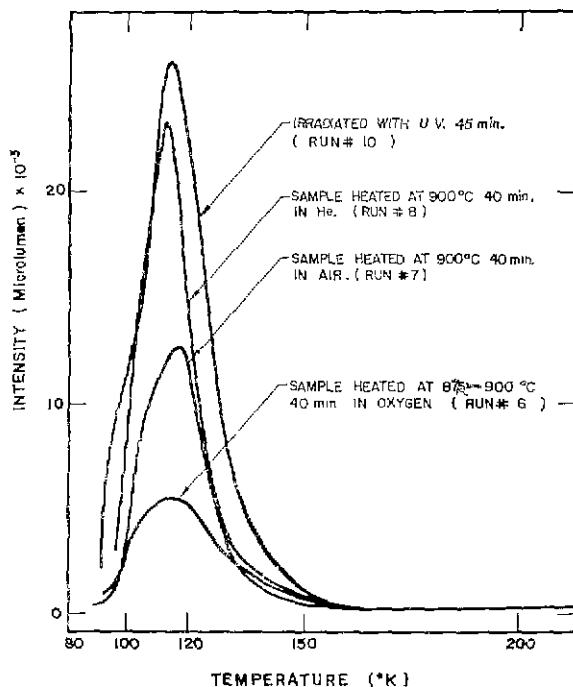

Fig. 12. Glow curve of ZnO irradiated with U. V. for 45 min. (RUN #6, 7. 8 and 10)

tion, these impurity levels might act either as retrapping centers or as secondary emittinge enters. In either case the net result would be a distortion of the glow curve.

With higher degrees of irradiation the concentration of electrons trapped at intrinsic centers would be high enough to wash out the effect of secondary trapping and thus restore a normal symmetrical glow curve. This is borne out by the fact that the curves obtained after 45 minutes of ultraviolet irradiation tend to be more symmetrical in nature (Figures 4 and 5).

The dependence of intensity on ultraviolet irradiationtime for zinc oxide specnimes annealed at various conditions prior to irradiation at 83°K is shown in Figure 13. All of the curves show a maximum and then give indication of decreasing to a constant value with longcer exposure times. The decrease in intensity is due to a kinetic equilibrium between the electrons being trapped and the electrons being freed rather than the complete filling of the trads to some stable energy level. At the maximum, the number of electrons being excited by ultraviolet radiation equals the number of electrons being freed from the traps. At longer exposure times, the numbers of electrons being
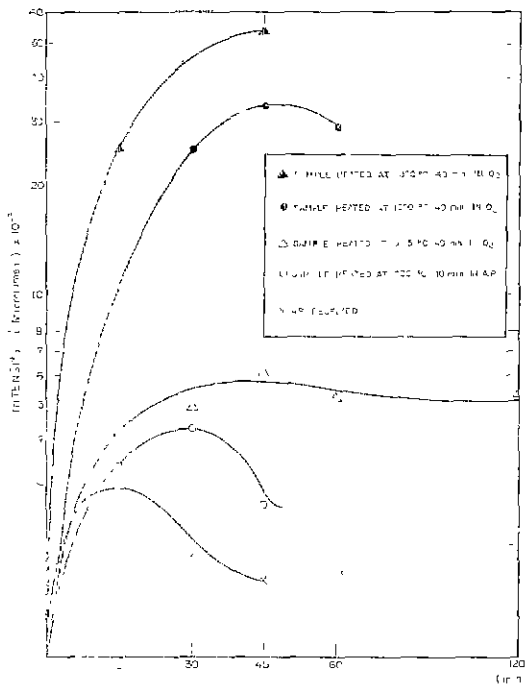
freed is greater than the number of el ectrons being excited by the radiation (since most of the electrons have already been excited to the trap level) and hence there is a lower concentration of electrons in the trap level than before to satisfy this rate of exchange.

The average peak temperature of all ZnO runs with a spnecimen weight of 300mg. is 115°K and this agrees in part with the results of other investigators. Heiland, Mullwoand Stöckmann[8] found a large peak at 120°K and a minor peak at 185°K. Reboul[9] reported a single peak at 150°K. These disciepencies may be due in part to a difference in the weight of the specimen employed. As shown in Table II. the specimen weight was 300mg. for all runs with the exception of run no. 13B where a 1000mg. specimen was used. The glow curve for this run is shown in Figure 10 and it can be seen that a single peak occurs at 145°K in agreement with the deta of Reboul[9].

Another series of experiments was carried out to determine the dependence of thermoluminescence on the oxygen partial pressure of the atmosphere employed in the prior annealing treatment. Figure 9 shows glow curves for specimens annealed at 1100°C for 40 minutes in air and oxygen and then irradiated in ultraviolet radiation for 45 minutes at the temperature of liquid nitrogen. The peak temperatures are in good agree-
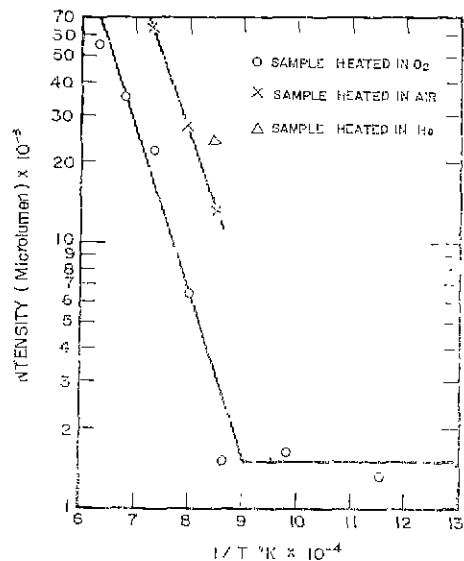

Fig. 13. Intensity vs U. V. radiation time for ZnO

Fig. 14. Intensity vs I/T (T is sample (heated temperature)

Table III. Summary of Activation energies for zinc oxides

Specimen Number	Run Number	Annealing Temperature (°C)	Annealing Atmosphere	Peak Temperature (PK)	Temperature at $I_{max}/2$ (°K)	Activation Energy (ev)
2	2	200	Air	100	97	0.12
2	2A	200	Air	110	94	0.09
2	2B	200	Air	113	100	0.14
3	3	500–520	O_2	111	103	0.19
4	4	600–620	O_2	105	95	0.13
5	5	740–760	O_2	111	102	0.16
6	6	875–900	O_2	118	102	0.10
7	7	900	Air	118	100	0.09
8	8	900	He	115	105	0.16
9	9	975	O_2	128	107	0.09
9	9A	975	O_2	121	103	0.09
9	9B	975	O_2	117	105	0.13
9	9C	975	O_2	119	107	0.14
9	9D	975	O_2	118	106	0.14
10	10	100	Air	115	104	0.14
11	11	1100	O_2	122	103	0.09
12	12	1100	Air	120	111	0.19
13	13	1200	O_2	118	100	0.09
13	13A	1200	O_2	116	98	0.08
14	14	1300	O_2	124	105	0.0
14	14A	1300	O_2	119	111	0.21

ment but the intensity of the peak for the specimen annealed in air is about a factor of 3 greater than that for the oxygen anneal. Further evidence for the marked dependence of peak intensity on oxygen partial pressure is shown in Figure 12 for specimens which received identical treatment with the exception of the annealing atmosphere. As in the previous case, the peak temperatures are in agreement but the intensity of the peak for the air anneal is a factor of 8 greater than that of the oxygen anneal and the helium anneal produces an intensity greater than that obtained in oxygen by a factor of about 15.

These results clearly indicate a dependence of thermoluminescence intensity on oxygen partial pressure; that is, on the concentration of non-stoichiometric point defects.

The temperature dependence of thermoluminescence intensity may be expressed by the following well-known relationship

$$I = I_0 \exp(-E/KT)$$

Figure 14 is a plot of logarithm of peak intensity versus reciprocal of the absolute temperature for the three annealing atmospheres and an ultraviolet irradiation time of 45 minutes. Since the points at 900°C and above are best represented by a straight line, the intensity is exponentially dependent on reciprocal annealing temperature in this range. The activation energy calculated from the slopes of the curves is 1.24 ev for both oxygen and air. Below 900°C the peak intensity for specimens annealed in oxygen is independent of the annealed in oxygen is independent of the annealing temperature. Therefore, the thermoluminescence behavior is entirely defect controlled in the temperature range 900~1300°C.

The non-stoichiometric defect responsible for defect controlled conductivity in ZnO may be an oxygen ion vacancy with two trapped electrons. If this is the case, the activation energy of 1.24ev obtained in this investigation is associated with thergy to create the vacancy and two trapped electrons. This defect mechanism for thermoluminescence has been reported for thoria[1] and alpha niobium pentoxide[2]. In both of these cases the non-stoichiometric defect involved to explain physical behavior is also the oxygen ion vacancy with two trapped electrons.

From Equation(1) the activation energy of trap can be calculated for the specimens and the results are shown in Table III. The average activation energy of specimens annealed in oxygen is 0.12ev, in air the average is 0.13ev, and in helium the result of a single run is 0.16ev. The average activation energy for specimens annealed in oxygen in the range 900~ 1300°C is 0.12ev and for temperature less than 900°C the average trap is 0.15ev. It is felt that the agreement in activation energies is good. Therefore, the same non-stoichiometric defect is probably responsible for thermoluminescence in all of the ZnO specimens.

4. CONCLUSIONS

The glow curves of ZnO exhibit a single peak at an average temperature of 115°K. peak reported in anearlier investigation was shown to be the result of the weight of the sample employed. The dependence of peak intensity on the time of ultraviolet irradiation shows maximum for a given annealing treatment and atmosphere. A probable explanation for this behavior is the establishment of kinetic equilibrium between the electrons being trapped and the electrons being freed rather than the complete filling of the traps to a stable energy level.

The thermoluminescence behavior of ZnO is dependent on the partial pressure of oxygen in the annealing atmosphere at temperatures above 900°C, that is, the concentration of non-stoichiometric point defe-

cts. The peak intensity is exponentially dependent on $1/T$ and the associated activation energy is 1.24ev. The non-stoichiometric defect responsible for this behavior is probably an oxygen ion vacancy with two trapped electrons. The average activation energy for all runs is 0.13 ev and it is felt that the same trap is present in all the ZnO samples.

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