

Researches on the Activation Energy of (Ba, Sr) O by Electron Bombardment

By

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ABSTRACT

When (Ba, Sr)O is bombarded by electrons, it is found that the resistance *versus* accelerating voltage curve shows a trough at some accelerating voltage. From the estimation of the kinetic energy of an incident electron which causes the trough change, it has been found that the optical activation energy required to remove an electron from the impurity level to the conduction band is about 3.35 ev. This agrees with the value as estimated roughly from thermionic data.

By this method may be obtained the energetic structure of such a substance that cannot be investigated by spectroscopic method.

To get more accuracy, however, the results obtained by this method must be compared with those obtained by the spectroscopic method for the well-known substances.

Moreover, it has been found that the impurity level plays an important role in the phenomenon of secondary emission of excess type impurity semiconductor.

1. Introduction

The thermionic work function of (Ba, Sr) O has been measured by many workers since 1924 (1). But the thermal activation energy Δe has not been measured because it is not distinct whether the value obtained from the temperature dependence of conductivity is $\Delta e/2$ or Δe . Also, optical activation energy has not yet been measured because of the difficulty in the treatment of a sample. Thus we have attempted to get its activation energy by electron bombardment.

2. Experiment

(1) Apparatus

The apparatus used in our experiment is shown in Fig. 1. The sample was made by winding 16 turns of each of two tungsten wires, about 0.01 cm in diameter, on the cylinder of insulating material about 0.2 cm in diameter and about 3.5 cm in length, and coating with (Ba,

indicating the sample potential, i. e. accelerating voltage. The parallel resistance was inserted so that none of the incident current did flow through the bridge circuit. All the measuring instruments were supported with insulating materials in order to prevent the leakage current.

(2) *Procedure*

Emitter's filament was fired after biasing the grid -30 volts so that none of the electron beam was incident. After the resistance of the sample, that was decreased by radiation from the emitter, had reached to equilibrium state, the sample was bombarded by electron beam for two minutes. Since it required 15~25 seconds to measure the resistance of the sample, the value after 30 seconds was recorded. The bridge circuit was open, during the bombardment, not to scale out. The same procedure was repeated by altering sample voltage after the resistance of the sample reached to equilibrium state. Thus it required 90~120 minutes for one series of observation to be finished. The vessel was kept evacuated at about 10^{-6} mm Hg by means of a liquid air trap.

(3) *Results*

(i) The resistance of the sample *versus* the accelerating voltage curve shows a minimum at about 1.5 volts in the case of ThW emitter (Fig. 3) and at about 0.2 volts in the case of Oxide emitter (Fig. 4) and then increases up to the value in the case of non-bombardment with increasing accelerating voltage. Above 2.0 volts in the former case, and above 0.7 volts in the latter one, the resistance does not change by the electron bombardment.

This trough of the resistance curve seems to depend upon the excitation of electrons from a bound state to the conduction band. And the kinetic energy of an incident electron which causes the trough gives approximately the optical activation energy from the bound state to the conduction band. We shall call this quantity $h\nu_{\max}$ (cf. Discussion). Now $h\nu_{\max}$ is given by substituting the observed value of V into the following equation (2):

$$h\nu_{\max} \equiv \frac{1}{2}mv^2 = V - i_s r_A - i_s r + \Psi_A - \Psi_C, \text{ (ev)} \quad (1)$$

where V : reading (in volt) of accelerating voltage meter when the trough occurs,

i_s : sample current (ampere) (cf. Results (ii)),

r_A : internal resistance of ammeter = 1013 Ω ,

r : series resistance = $0.5 \times 10^6 \Omega$,

Ψ_A : work function of sample = 4.54 ev (cf. Discussion),
 Ψ_C : work function of emitter : 3.00 ev for ThW and 1.35 ev for Oxide (cf. Discussion).

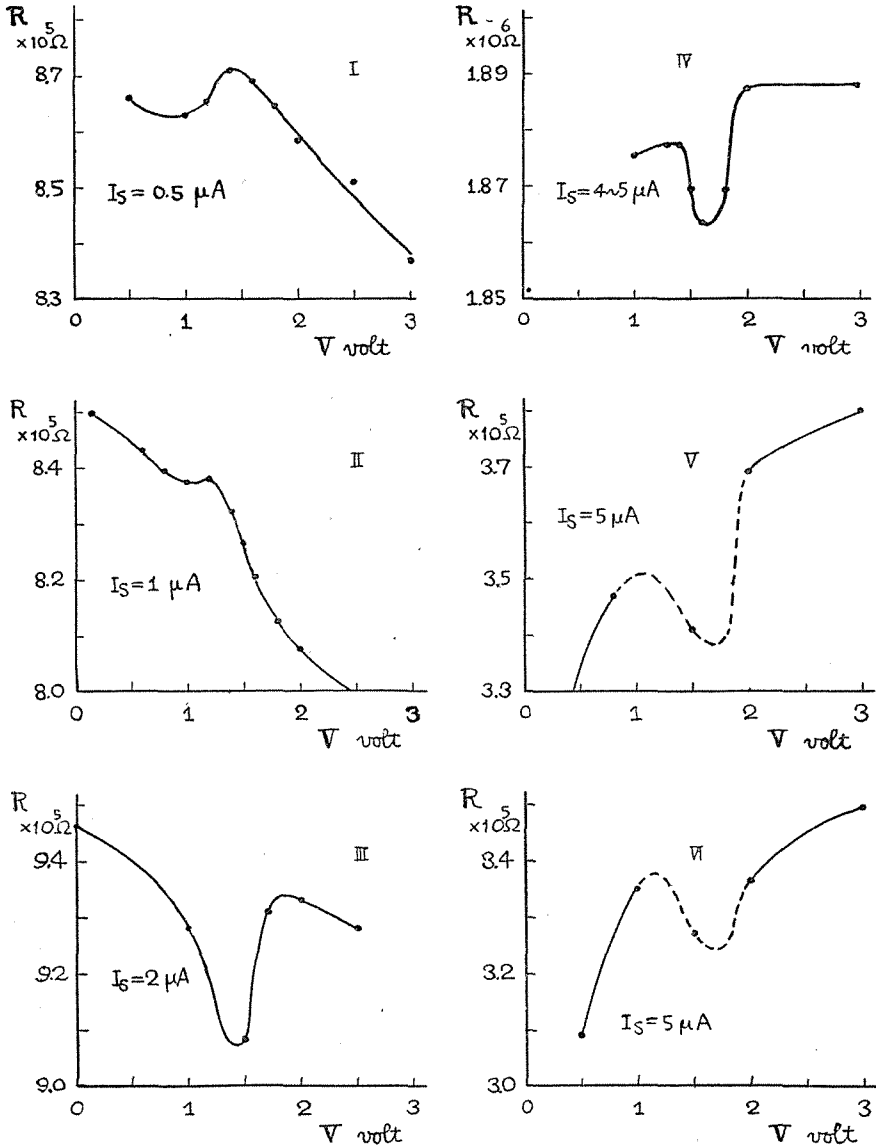


Fig. 3.

R : resistance of the sample.
 V : reading of accelerating voltage meter.
 I_s : incident current through the sample.

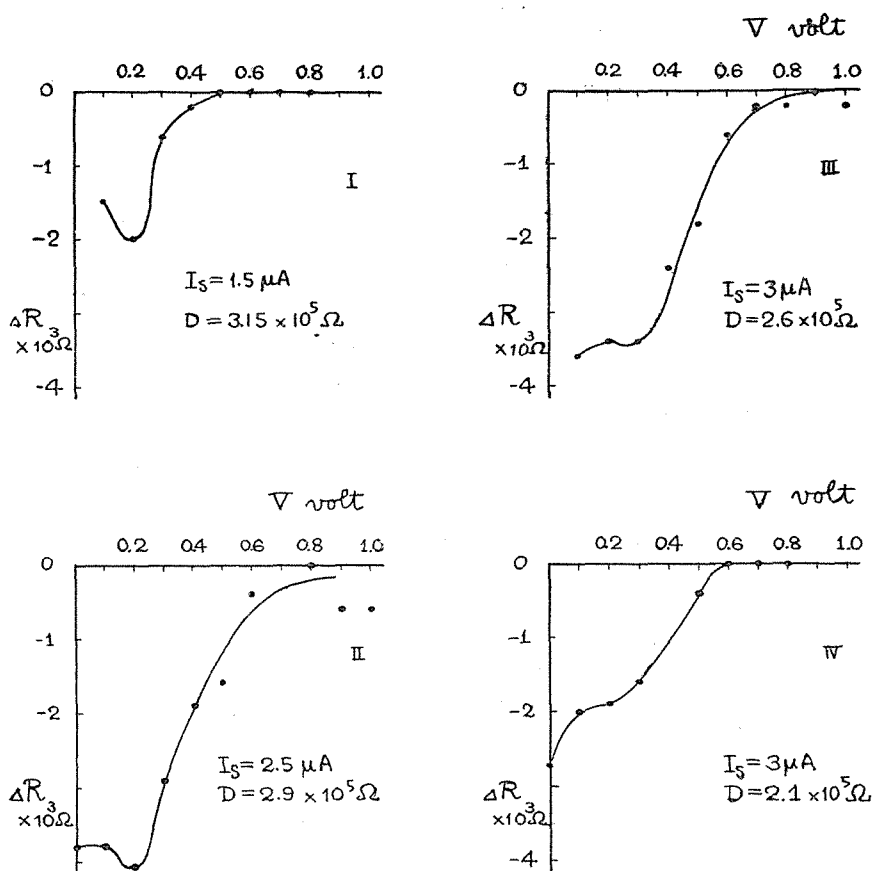


Fig. 4.

ΔR : decrement of the resistance.
 D : dark resistance of the sample.

The observed values of V and the calculated values of $h\nu_{max}$ are given in the following Table I.

TABLE I.

Emitter	i_s ($\times 10^{-6}$ A)	Observed values of V (volt)	$h\nu_{max}$ (ev) (calculated)
Th W	0.5	0.9	2.19
"	1.0	1.0	2.04
"	2.0	1.45	1.99
"	4.0~5.0	1.65	1.19
"	5.0	1.7	0.74
Oxide	1.0	0.18	2.87
"	1.5	0.2	2.64
"	1.7	0.2	2.54
"	2.5	0.2	2.14
"	3.0	0.23	1.91

The curve of $h\nu_{\max}$ versus the sample current decreases with increasing sample current both in the cases of ThW emitter and of Oxide emitter (Fig. 5). By extrapolation from this curve we have obtained the value

$h\nu_{\max} \sim 3.35$ ev in the latter case (cf. Discussion).

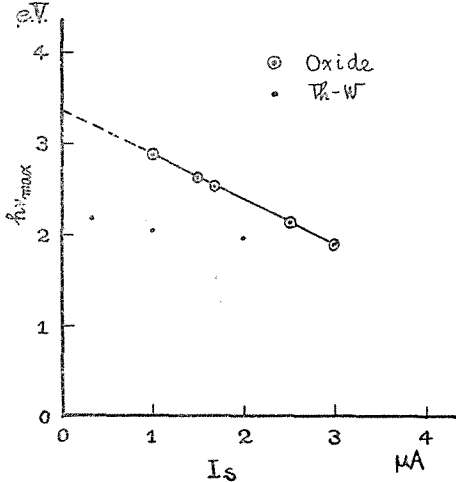


Fig. 5.

(ii) In order to explain the question why the resistance does not change above 2.0 volts (ThW) or 0.7 volts (Oxide), we observed the resistance and secondary emission against the accelerating voltage simultaneously.

The blackened nickel plate, whose area is 1/6 of that of the sample, was placed in the same plane of the surface of the sample and perpendicular to the incident beam. The plate current i_n in case when the same

voltage as the sample voltage was supplied, was measured together with the sample current i_s . Thus, we have obtained the results that

(a) $6i_n > i_s$,

(b) $\delta = \frac{6i_n - i_s}{6i_n}$ versus accelerating voltage curve shows the same

behaviour as the resistance curve (Fig. 6).

Thus the reason why the resistance does not change above the given voltage is that bound electrons are not excited to the conduction band but emitted as secondary electrons. It seems therefore that the impurity level (cf. the next section) plays an important role for the secondary electron emission from (Ba, Sr) O.

(iii) After two or three series of the bombardment the resistance begins to decrease monotonously and is independ-

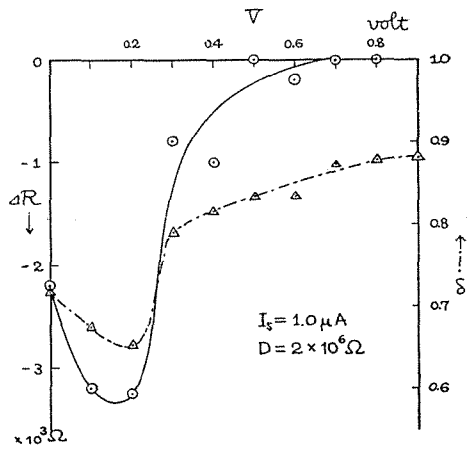


Fig. 6. δ = yield of secondary electron.

ent of the accelerating voltage and then the surface of the sample has been blackened.

Also, as soon as a liquid air vessel is removed, it is immediately blackened. Therefore it seems that adsorbed diffusion pump oil on the surface is carbonized by the electron bombardment.

(iv) In spite of the fact that the dark resistance of the sample ranges over $10^5 \sim 10^6$ ohms, the decrement of resistance is about the same quantity in each case and depends only upon the incident current. It seems that this phenomenon depends only upon the energetic structure of surface layers.

3. Comparison with the optical activation energy estimated from thermionic data

It has been known that the thermal activation energy, required to excite thermally an electron from the impurity level to the conduction band, is about 1.4 ev. Therefore the optical activation energy, roughly estimated from the above value, is about 3.5 ev. This agrees approximately with the value 3.35 ev which have been obtained in the present experiment. Thus we conclude that the trough of resistance curve depends upon the excitation of electrons from the impurity level to the conduction band by the electron bombardment.

For the work function of (Ba, Sr) O, various different values have been obtained by many workers. Nijboer (3) attempted to explain this fact by assuming that the number of impurity levels is greater than that of electrons available. He obtained the equilibrium state of crystal from the condition that the free energy of crystal is minimum. According to his results work functions ψ_1 and ψ_2 corresponding respectively to the cases of good activation and bad one, are given as follows:

$$\psi_1 = \frac{\Delta\epsilon}{2} + \phi, \quad \psi_2 = \Delta\epsilon + \phi,$$

where $\Delta\epsilon$ is the thermal activation energy and ϕ is the width of the conduction band. Adopting the same model, we obtained the same results by the entirely statistical method (cf. Appendix below).

Kawamura (1) has found, by the method of Richardson's line, that the work function of (Ba, Sr) O ranges over 1.0~1.7 ev in various cases. Thus, putting

$$\left. \begin{aligned} \Delta\epsilon/2 + \phi &= 1.0 \text{ (ev),} \\ \Delta\epsilon + \phi &= 1.7 \text{ (ev),} \end{aligned} \right\}$$

he has obtained the results that

$$\left. \begin{aligned} \Delta\varepsilon &= 1.4 \text{ (eV)}, \\ \phi &= 0.3 \text{ (eV)}. \end{aligned} \right\} \quad (2)$$

Now it has been observed (4) that the surrounding ions do not move during an electron's removal from an impurity center by the absorption of kinetic energy of an incident electron. Also this fact has been predicted from the probability calculated by the quantum theory of molecules (5). Therefore, we have (6)

$$h\nu_{\max} - \Delta\varepsilon \approx \frac{e^2}{2R} \left(\frac{1}{\kappa_0} - \frac{1}{\kappa} \right),$$

where κ_0 is the dielectric constant for high frequency, κ the dielectric constant for electrostatic field, and R the radius of impurity atom.

Since the depth of the potential hole with this model is $e^2/\kappa_0 R$ we shall have

$$h\nu_{\max} \sim e^2/2\kappa_0 R,$$

$$\Delta\varepsilon \sim e^2/2\kappa R.$$

Assuming that $\kappa_0 \sim 4$, $\kappa \sim 10$ for (Ba, Sr) O which seem to be probable, we obtain

$$h\nu_{\max} \sim \frac{10}{4} \Delta\varepsilon. \quad (3)$$

Substituting Eq. (2) into Eq. (3) we have

$$h\nu_{\max} \sim 3.5 \text{ (eV)}. \quad (4)$$

4. Discussion

(1) We assumed that the value of $h\nu_{\max}$, i. e. the kinetic energy of an incident electron which causes the trough change gives approximately the optical activation energy. To know the more strict meaning of $h\nu_{\max}$ we must take into account the fact that incident electrons distribute according to the Maxwellian distribution law and that the conduction band has its width. Thus we shall have a quantitative relation among the short wave edge, the long wave edge and $h\nu_{\max}$. The discussion on such a relation is now in progress.

(2) In calculating $h\nu_{\max}$ by Eq. (1), the following three assumptions are made:—

(a) Initial velocity distribution of incident electrons is assumed to show a maximum at zero velocity. Since incident electrons actually distribute according to the Maxwellian distribution law the maximum would be at about 0.0869 ev. This, however, is of the order of lattice vibration, i. e., the order of $1/40 \sim 1/20$ ev and so can be neglected.

Also the hump of surface barrier that accelerates the emitted electrons is neglected. But it seems to have an appreciable height in the case of ThW emitter, as we shall show later.

(b) The work function of tungsten electrodes (4.54 ev (7)) is taken as that of the sample, since the electrodes expose from the Oxide surface. Otherwise the reasonable value of $h\nu_{\max}$ cannot be obtained simultaneously both in the cases of ThW and Oxide emitters.

The work function of ThW emitter (3.00 ev) is taken from the table (7). It corresponds to the case of $\theta = 0.812$. That of Oxide (1.35 ev) is the intermediate value of Kawamura's data (cf. the previous section). Therefore, the obtained value of $h\nu_{\max}$ has uncertainty of about ± 0.35 ev in both cases. To obtain the more accurate value, the contact potential difference between the sample and the emitter should be measured.

(c) The effect of charging up the sample is neglected. It, however, should be estimated as for the well-known substances.

(3) It seems to depend upon the hump of surface barrier and direct heating voltage that the value of $h\nu_{\max}$ is smaller in the case of ThW than in the case of Oxide. Therefore the data in the latter case are used to get $h\nu_{\max}$.

(4) The decrease of the $h\nu_{\max}$ versus the incident current curve is more rapid in the case of Oxide than in the case of ThW. The fact shows that this decrease cannot be explained only by the lattice vibration of the sample. It seems to be probable that, externally applied voltage is decreased in the case of Oxide, since the mean work function of the sample is increased by the production of WO ($\psi = 9.2$ ev (8)) on the sample electrodes. And it seems that the oxygen which produces WO, becomes to be dissociated from the CO₂ gas, that is evaporated from the Oxide emitter, and adsorbed on the electrodes. According to this assumption it seems to be reasonable that $h\nu_{\max}$ decreases with the increasing incident current, since the production of WO increases with the increasing incident current. This should be tested by measuring the actual contact potential difference in the above case.

(5) The fact that the resistance curve closely agrees with the secondary emission curve, seems to suggest how interactions occur between the

low velocity electron and the crystal. From this point of view, it seems to be naturally comprehensible that the effect of the bombardment can be observed after 30 seconds.

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Appendix

The feature of this derivation is that Fermi level, ϵ' , is obtained and therefore is easy to get the emission formula. Calculating by the usual δ -function method (9) we obtained the following results:

$$C e^{\frac{\epsilon'}{kT}} (kT)^{\frac{3}{2}} \sqrt{\pi}/2 = N e^{-\frac{\Delta\epsilon + \epsilon'}{kT}} - (N_0 - N), \quad (1)$$

where $C \equiv 4\pi(2m^*)^3/k^3$ and m^* is the effective mass of electron, N_0 the number of impurity states, N the number of electrons available at 0°K , ϵ' the Fermi level at $T^\circ\text{K}$, $\Delta\epsilon$ the thermal activation energy. Energy zero is taken at the bottom of conduction band. The quantity on the left-hand side of Eq. (1) is the number of electrons that have been excited from the impurity level. Then, the following two limiting cases present themselves:—

(i) If $N_0 - N \ll C e^{\frac{\epsilon'}{kT}} (kT)^{\frac{3}{2}} \sqrt{\pi}/2$, which holds in the case of good activation, we have approximately

$$C e^{\frac{2\epsilon'}{kT}} (kT)^{\frac{3}{2}} \sqrt{\pi}/2 = N e^{-\frac{\Delta\epsilon}{kT}}.$$

Thus,

$$\epsilon' = -\frac{\Delta\epsilon}{2} + \frac{kT}{2} \log \frac{N \cdot 2}{C (kT)^{\frac{3}{2}} \sqrt{\pi}}. \quad (2)$$

Therefore the thermionic current is

$$i = A_1 N^{\frac{1}{2}} T^{\frac{5}{4}} \exp\left(-\frac{\phi + \Delta\epsilon/2}{kT}\right), \quad (3)$$

where $A_1 \equiv (2/h^3)^{\frac{1}{2}} (2\pi m^*)^{\frac{1}{2}} k^{\frac{5}{2}} e_0$, and e_0 is the electronic charge and ϕ the width of conduction band. Hence, the work function as obtained from the slope of Richardson's line is

$$\psi_1 = \phi + \Delta\epsilon/2. \quad (4)$$

(ii) If $N_0 - N \gg Ce^{\frac{\epsilon'}{kT}} (kT)^{\frac{3}{2}} \sqrt{\pi}/2$, which holds in the case of bad activation, we have approximately

$$N_0 - N = N \exp\left(-\frac{\Delta\epsilon + \epsilon'}{kT}\right),$$

and consequently

$$\epsilon' = -\Delta\epsilon + kT \log \frac{N}{N_0 - N}. \quad (5)$$

Therefore

$$i = A_2 \frac{N}{N_0 - N} T^2 \exp\left(-\frac{\phi + \Delta\epsilon}{kT}\right) \quad (6)$$

with $A_2 \equiv 4\pi m^* k^2 e_0 / h^3$, and consequently

$$\psi_2 = \phi + \Delta\epsilon. \quad (7)$$

REFERENCES

1. H. Kawamura, Proc. Phys. Math. Soc. Japan **17** (1943), 175.
2. W. Heinze, ZS. f. Phys. **109** (1938), 459.
P. W. Bridgman, Phys. Rev. **11** (1919), 306.
3. J. H. de Boer, and W. C. Van Geel, Physica **2** (1935), 286.
B. R. A. Nijboer, Proc. Phys. Soc. **51** (1935), 575.
4. R. Whiddington and H. Jones, Phil. Mag. **6** (1928), 889.
J. Franck, Trans. Faraday. Soc. **21** (1925), Part II 536.
E. Condon, Phys. Rev. **28** (1926), 1182.
5. N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collision* (1933), 209.
6. N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (1940), 160.
7. *International Critical Tables* (1928), VI 55.
8. R. H. Fowler, *Statistical Mechanics* (1936), 364.
9. F. Seitz, *The Modern Theory of Solids* (1940), 186.