Electron-Bombardment-Induced Dissociation of Alkaline Earth Oxides*

P. Wargo† AND W. G. Shepherd
University of Minesota, Minneapolis, Minnesota
(Received December 14, 1956)

The oxygen evolution induced by electron bombardment of alkaline earth oxides has been directly observed by means of an omegatron mass spectrometer. Threshold energies for the process have been determined as 9.5±0.5 ev, 14.0±0.5 ev, and 16.9±0.5 ev for BaO, SrO, and MgO, respectively. It is found that the efficiency of the process is in all cases proportional to the square of the current density at the target. It is suggested that a two-step electron excitation in the solid is involved. In the case of SrO the use of a radioactive isotope of strontium provided a monitor for the release of the metal from the target. The energy dependence of the evolution of oxygen and strontium suggests that there are two processes, one predominating at low energies and the other at higher energies. An evolution of oxygen at a threshold energy of approximately 5 ev was observed for a variety of targets. The behavior of this evolution suggested that a desorption process was involved.

INTRODUCTION

MIXTURES of BaO, SrO, and CaO are commonly used as the emitting material of the cathodes of thermionic vacuum tubes. It has been established by many investigators[1-4] that during operation these materials sublime from the hot oxide-coated cathode onto other electrodes, and it has been inferred that they subsequently decompose under electron bombardment. Other alkaline earth oxides such as BeO and MgO are commonly used as the emitting surfaces of secondary emission dynodes. That the decomposition of the oxide may be a limiting factor in the life of the dynodes has been established by Woods and Wright[3] and by Wargo, Haxby, and Shepherd.[5]

In the course of studies in which radioactive tracer techniques were used to determine the nature of the evaporation products from oxide-coated cathodes, Leverton and Shepherd[2] found that strontium which had evaporated from the cathode to an anode disappeared when the anode was subjected to electron bombardment. This effect was later verified by Anderson[6] and Yoshida, Shibata, Igarashi, and Arata.[7]

Jacobs[8] concluded that the threshold energy for dissociation under electron bombardment of FeO, CuO, NiO, MoO₃, and WO₂ was equal to the heat of formation of the compound. He bombarded the particular oxide with electrons from a cathode operating under temperature-limited conditions, and took for the threshold for dissociation the potential of the target at which a drop

in the cathode electron emission occurred. He assumed that the oxide was being decomposed by the bombardment and that the evolved oxygen "poisoned" the cathode. It was suggested that when the electron reached the "critical kinetic energy" equal to the heat of formation, the metallic oxide could be dissociated.

Using similar techniques Metson[9] gave 5.56 ev as the dissociation threshold of BaO under electron bombardment and compared this to the heat of formation (5.78 ev/molecule). Metson found that the "poisoning" of the cathode, which he attributed to the apparent dissociation of the oxide, disappeared after prolonged bombardment of the oxide. At this point he assumed that he had completely dissociated the BaO that had been initially evaporated to the target. Upon raising the target potential, he found that "poisoning" could again be observed at a threshold of 9.4 ev, which he attributed to the dissociation of BaCl₂ (H=8.92 ev/molecule) which had evaporated from the cathode.

Similar experiments by Wright and Woods[3] showed no dependence of the threshold energy upon the heat of formation. They found thresholds of 4 ev and 5 ev for evaporated layers of BaO and BaCl₂, respectively, which they ascribed to the energy of formation of excitons which subsequently dissociated thermally, releasing one or both constituents from the solid.

Using the same technique, Amakasu et al.,[4] also found a threshold of 4 ev which they attributed to the dissociation of BaO. Their data also showed that on bombardment of the oxide with 8-ev electrons an immediate decay of the emission from the electron source was observed, but that after prolonged bombardment the emission eventually recovered.

All of the above work has a common limitation, namely, the lack of positive identification of the dissociation products.

In a simple two-body process, the kinetic energy which can be transferred from an incident electron directly to a molecule is insufficient to produce dissociation unless the electron energy is of the order of 10 kev. Since reported thresholds are of the order of a

* This work was carried on under the sponsorship of the Signal Corps Engineering Laboratories, Fort Monmouth, New Jersey.
† Now at the General Electric Research Laboratories, Schenectady, New York.
[1] L. B. Headrick, and E. A. Lederer, Phys. Rev. 50, 1094 (1936).
[2] W. F. Leverton, and W. G. Shepherd, J. Appl. Phys. 23, 797 (1952).
[3] J. Woods and D. A. Wright, Brit. J. Appl. Phys. 4, 56 (1953) and Proc. Phys. Soc. (London) B66, 1073 (1953).
[4] Amakasu, Imai, and Asano, Le Vide 10, 366 (1955).
[5] Wargo, Haxby, and Shepherd, J. Appl. Phys. 27, 1311 (1956).
[6] S. D. Anderson, M.S. thesis, University of Minnesota, 1954 (unpublished).
[7] Yoshida, Shibata, Igarashi, and Arata, J. Phys. Soc. Japan 9, 640 (1954).
[8] H. Jacobs, J. Appl. Phys. 17, 596 (1946).
[9] G. H. Metson, Proc. Phys. Soc. (London) B62, 589 (1949).

few electron volts, it appears necessary to postulate a process involving an energy exchange between the incident and lattice electrons, with a resultant dissociation and liberation from the solid.

In the present work, a set of experimental results are presented which, it is believed, shed new light on the nature of the mechanism of the dissociation of thin layers of SrO, BaO, and MgO under electron bombardment. The evolution of oxygen from the oxide under bombardment has been detected by a modified omegatron as described by Alpert and Buritz.[10] In addition, in the case of SrO, a radioactive tracer, Sr^{89} was included in the oxide in order that the evolution of metal could be observed.

EXPERIMENTAL

Apparatus

A diagram of the experimental apparatus is shown in Fig. 1. Five movable targets of DH 499 nickel were mounted on a wire as shown in the diagram. Three of the targets were coated with the oxides under investigation while two targets were left blank for purposes of control and calibration. By means of a magnet each target could be moved over the electron gun for bombardment. The electron gun used for bombardment of the targets consisted of a disk-type triple oxide-coated cathode, a grid for current control, and an anode support ring to insure accurate duplication of the position of the targets over the cathode after radioactivity measurements. For the latter measurements, the targets were moved to the end of the tube where the radioactivity of the target could be counted through a thin Kovar window. The window was 0.0015 in. thick and transmitted approximately 80% of the 1.5-Mev β emission of Sr^{89}.

The main tube was connected to an omegatron by means of a piece of glass tubing about 0.5 in. in diameter and about 7 in. long. The tubing was made long to separate the bombarding electron gun from the magnetic field of the omegatron, thus preventing serious curvature of the electron trajectories.

The targets coated with the various oxides were prepared by methods dictated by necessity or convenience. In the case of SrO, it was desired to include radioactive Sr^{89} (half-life of 55 days). Because of the relatively low efficiency for the dissociation, it was necessary to make the SrO films very thin so that small changes in the radioactivity of the sample could be easily detected. The SrO targets were prepared by placing a drop of $Sr(OH)_2$ solution on a blank Ni target and evaporating to dryness. The radioactivity of the sample was measured and compared to the radioactivity of a standard sample prepared from the same batch and containing a known quantity of strontium. Additional $Sr(OH)_2$ could be added to the target until the radioactivity indicated that the average thickness of the
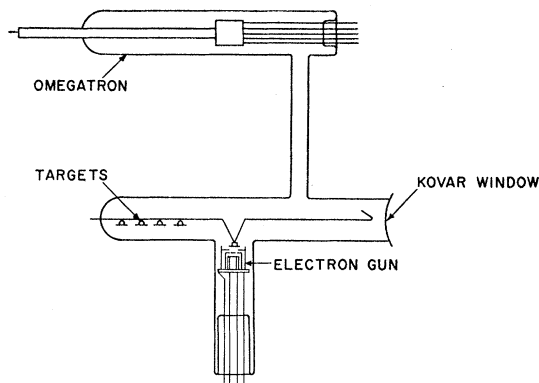

FIG. 1. Schematic diagram of the experimental tube used to investigate the electron bombardment induced dissociation of alkaline earth oxides.

$Sr(OH)_2$ layer was of the order of 100 to 200 A. Evaporated films of SrO were not used, since there is evidence that the evaporation product from SrO under certain conditions may be a mixture of the metal and the oxide.[11-13] The targets were inserted in the experimental tube, and the $Sr(OH)_2$ was converted to the oxide by heating to 1000°C in vacuum.

The BaO targets were prepared by painting a suspension of $BaCO_3$ in nitrocellulose onto the nickel backplate to a thickness of approximately 1000 A and subsequently converting to the oxide by heat treatment in vacuum.

The MgO targets were prepared by heating a 1.7% Mg-Ag alloy in an oxidizing atmosphere. The thickness of the films formed in this fashion was also of the order of 1000 A.

All tube parts were carefully cleaned and fired in vacuum or hydrogen, and the glass envelope was subjected to a rigorous cleaning procedure. The tubes were evacuated and outgassed by baking at 400°C for periods up to 20 hours. After bake-out the thorium-misch metal getter was outgassed, and the bombardment cathode was converted. The targets were not exposed to this cathode during breakdown. All metal parts were subsequently outgassed by rf heating, and in particular, the targets were heated to 1000°C (brightness temperature) both to outgas the metal backing and to convert the hydroxide or carbonate to the oxides. In the case of the MgO target the outgassing temperature was limited to 750°C. Electron gun parts were outgassed by electron bombardment where possible.

The getters employed in the tube were composed of 80% thorium, 5% aluminum, and 15% misch metal (a mixture of rare earths) sintered onto a molybdenum ribbon which could be heated by passage of current. This getter was outgassed at 1100°C at a pressure of approximately 1×10^{-7} mm and thereafter could getter

[10] D. Albert and R. S. Buritz, J. Appl. Phys. 25, 202 (1954).

[11] R. H. Plumlee and L. P. Smith, J. Appl. Phys. 21, 811 (1950).
[12] L. T. Aldrich, J. Appl. Phys. 22, 1168 (1951).
[13] I. Pelchowitch, Philips Research Repts. 9, 42 (1954).

effectively, at 350 to 500°C, all the gases encountered in the tubes except helium.

Method

Before all tests the cathodes of the tubes were stabilized by drawing electron current to a plain nickel target for a period of four days, in order to activate the cathode and to allow any excess volatile materials to evaporate from the cathode prior to its use for bombardment. The getters were operated at the gettering temperature during the aging period to prevent accumulation of gas.

The omegatron was operated under conditions similar to those described by Alpert and Buritz.[10] The ion current was measured by a vibrating reed electrometer and recorded as a function of the oscillator frequency. The output ion current for the O_2^+ peak was calibrated as a function of the oxygen pressure in the system and was found to be linear in the range from 5×10^{-7} to 5×10^{-6} mm and to deviate slightly at higher pressures. It was found that an ion current of 3×10^{-10} ampere corresponded to an oxygen pressure of 1×10^{-6} mm. It is felt that the calibration is good only to $\pm 20\%$, since it was done against a type 1949 ionization gauge. The limit of detection of the over-all instrument was a pressure of the order of 5×10^{-11} mm. The dispersion of the instrument was such that ions of H_2O^+, NH_3^+ and O^+ could be separately detected, and the O_2^+ peak was well separated from that of N_2^+.

Immediately after the tube and omegatron were sealed from the vacuum system and put to test, the total pressure in the tube was of the order of 10^{-7} to 10^{-6} mm, consisting primarily of oxygen and water vapor, with traces of CO_2 and N_2 or CO. These gases were removed by operating the getter until the pressure fell to less than 10^{-9} mm.

When the aging period of the cathode was completed, the getter was turned off, and the "background" rate of evolution of gas was measured. During this time the electron beam was allowed to bombard a blank target

at 30 v and 5 ma of current (a density of 25 ma/cm^2). It was found that oxygen was evolved at a rate of approximately 10^9 atoms per sec which was sufficient to raise the pressure in the tube from 10^{-10} mm to about 10^{-9} mm in from ten to thirty minutes. Substantially no increase was observed in the partial pressure of H_2O or CO_2 which were present at pressures of approximately 10^{-10} mm. No other gases were observed so that if they were present, it could only be in quantities that were below the limit of detection. As time went on, the "background" evolution rate of oxygen decreased to a rate which was small compared to the rate of evolution of oxygen when an oxide was bombarded.

Results

Evolution of Adsorbed Gas

When a fresh target was placed over the gun and bombarded with the getter cold, it was found that the pressure in the tube rose to a pressure of 10^{-5} to 10^{-6} mm in a matter of a few minutes. This gas consisted mainly of oxygen and water vapor with CO_2 and CO also contributing. When the gas was gettered and the bombardment immediately repeated, it was found that the succeeding pressure increase was much smaller. After 20 to 30 minutes of bombardment the evolution disappeared and could not be re-established until twenty-four hours or more had passed without bombardment of the target. The following points led to the deduction that the effect was due to adsorbed gas:

(1) The effect was observed for both oxide-coated and plain nickel targets.

(2) After the initial evolution, the effect could not be reproduced quantitatively.

(3) After twenty-four hours or more during which the target had not been bombarded, the effect could again be observed.

Qualitative measurements showed the threshold bombarding electron energy required to produce the effect lay somewhere between 4 and 5 ev.

Evolution of Oxygen from SrO

The evolution of oxygen as a function of time of bombardment of an SrO target is shown in Fig. 2. The target was bombarded for one hour with the getter hot to insure the removal of adsorbed gas. At the end of the period the getter was cooled, and the rate of buildup of gas pressure in the tube was monitored. The amplitude of the O_2^+ peak measured after 75 minutes of bombardment at 500 v with a current of 0.6 ma (3.0 ma/cm^2) indicated that the oxygen partial pressure had risen to nearly 10^{-7} mm from an initial reading of 10^{-10} mm. The increase in the pressure of water vapor was of the order of 10^{-9} mm and was nearly obscured by the increase in the omegatron response to O^+, whose peak height was approximately one-fifth that for O_2^+. No
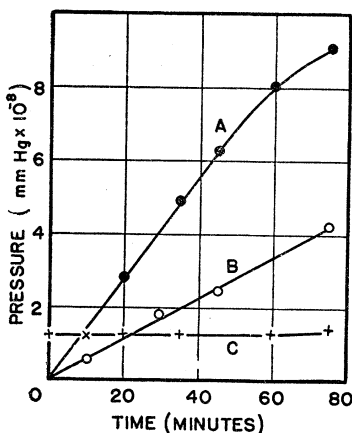
FIG. 2. The change in pressure of oxygen as a function of time of bombardment for (A) a SrO layer bombarded at a current density of 3 ma/cm^2 and an energy of 500 ev and (B) a SrO layer bombarded at a current density of 25 ma/cm^2 and an energy of 25 ev. Curve C shows the pressure of oxygen which had been developed from a previous bombardment as a function of time after bombardment ceased.
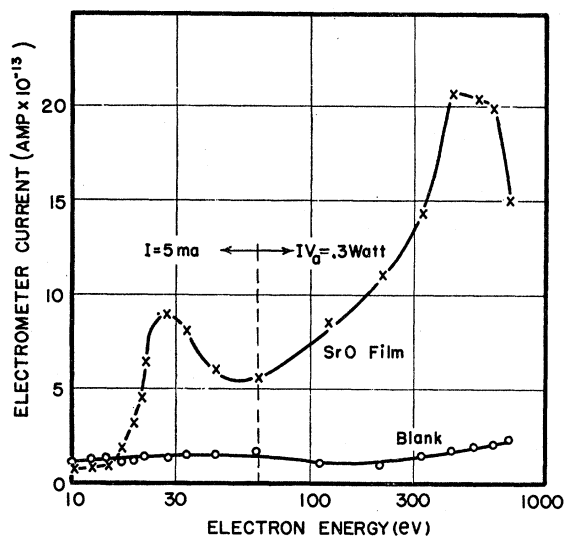
FIG. 3. Oxygen evolution produced by electron bombardment plotted as a function of the bombardment energy. The ordinates are the O_2^+ ion current from the omegatron. The upper curve was for a film of SrO and the lower curve for an uncoated nickel plate. The data to the left of the dashed vertical line are for a constant density of 25 ma/cm², those to the right for a constant bombardment power. The data are not normalized for constant current.

increases were observed in the CO_2^+, CO_2^{++}, CO^+, or N_2^+ peaks. A search over the higher mass region revealed nothing, and there was nothing between O_2^+ and CO_2^+. This was generally true throughout the experiments.

After the completion of a run the gas was gettered and the process repeated with a bombardment current of 5 ma at 25 volts with results similar to those above. Both sets of data are shown in the two upper curves in Fig. 2.

The effect of adsorption or desorption of gas by the glass walls of the tube or other surfaces was observed by allowing the oxygen pressure to build up to 1.3×10^{-8} mm as a result of bombarding SrO at 500 v and 0.6 ma for 10 minutes. After the bombardment was discontinued, the pressure in the tube was monitored for 75 min with the getter cold. During the monitoring period the target was held at cathode potential, but cathode current was drawn to the grid at a low potential. The results are shown in the lower curve of Fig. 2.

From these data it was deduced that for periods of time of less than one hour the effect of adsorption or desorption of gas by the tube walls, the cathode, and other components was negligible. In each subsequent tube this point was also checked.

Since the increase in gas pressure was linear with bombardment for at least one hour, a bombardment time of less than one-half hour was used, allowing a maximum pressure increase of 5×10^{-8} mm. This was partly dictated by a need to avoid emission difficulties with the cathode. In the work to be described on the evolution of oxygen from SrO, the actual bombardment

periods were twelve minutes long with a maximum oxygen pressure increase of 2.2×10^{-8} mm.

The procedure in observing the evolution of oxygen from SrO under electron bombardment was as follows: The SrO target was initially bombarded at 30 v and 5 ma for one hour, with the getter hot, in order to remove adsorbed gas. At the end of this period the mass spectrum of the gas in the tube was recorded over the range from mass 4 to mass 44. The getter was then cooled, and at the end of 12 min of bombardment under the same conditions, the mass spectrum was recorded. The getter was again heated until the mass spectrum showed that the evolved gas had been removed. With the getter cold, the bombardment was repeated at the same energy and current for twelve minutes, after which the mass spectrum was recorded to check for reproducibility. Only when the data could be repeatedly reproduced to within 5%, was the target potential set to a new value and the procedure repeated. The range of potentials covered was from zero to 700 v. Below 60 v the bombarding current was kept to 5.0 ma, while above 60 v the bombardment power was held at 0.30 w to maintain relatively constant target temperature.[14] At the end of a run on each sample, several points were repeated as an over-all check on reproducibility.

The increase in the oxygen peak height as a function of the bombarding energy for an SrO target is shown in Fig. 3. Also shown in the same figure are the results that were obtained when a typical blank nickel target was bombarded under the same condition. The oxygen peak height for this latter situation is a measure of the residual oxygen.

The reproducibility of the data for three different samples of SrO in the range of zero to 60 v is shown in a linear plot in Fig. 4. Similar agreement was found at
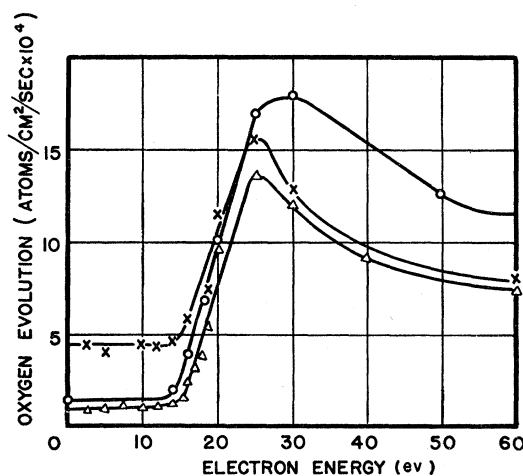

FIG. 4. Oxygen evolution is a function of electron energy for three SrO films. The bombardment current density was 25 ma/cm².

[14] Because of its proximity to the cathode, the target operating temperature was approximately 280°C. An input power of 0.30 watt raised the temperature to 300°C.
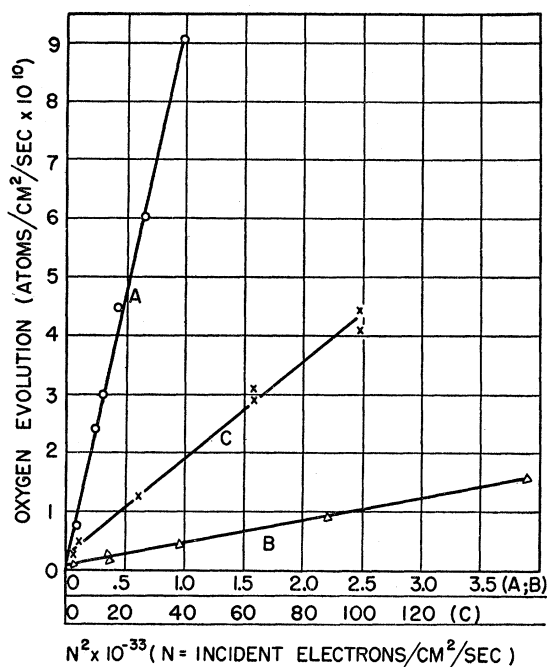
FIG. 5. Oxygen evolution as a function of the square of the number of electrons incident per cm² per sec on a SrO film. The energy of the incident electrons is, for curve A, 400 ev; for curve B, 150 ev; and for curve C, 25 ev. In each case the bombardment energy was limited to a maximum power of 0.3 w.

higher energies. The ordinate for these curves has been converted to number of atoms evolved per sec per cm² of bombarded area on the assumption that there is no readsorption or recombination of the liberated oxygen during the period of accumulation.

A significant feature of the data is the indication of two distinct energy-dependent processes. The low-energy process appears to have a threshold at approximately 14 ev. Below 14 ev the rate of evolution is relatively constant and comparable with the ultimate evolution when a plain nickel target is bombarded for long periods. This "background" evolution may arise from the cathode or from bombardment of the control grid.

The current density dependence of the evolution rate of oxygen was examined at three different energies; 25 ev, 150 ev, and 400 ev. In each case it was observed that the rate of evolution varied as the square of the bombarding current density. These data are shown in

TABLE I. Evolution of material from SrO bombarded with 200-volt electrons.

Current ma	Current density ma/cm²	Anode temp. °C	$10^{-9} \times$ No. of atoms evolved per cm² per sec	
			Strontium	Oxygen
1.5	7.5	300	1	16
2.5	12.5	350	1	41
5.0	25.0	550	16.0±3.5	162
10.0	50.0	700	391±39	652

Fig. 5 where the number of oxygen atoms evolved per cm² per sec is plotted as a function of the square of the number of incident electrons per cm² per sec. In these particular tests the maximum power input to the target was 0.30 w. It was subsequently found that the oxygen evolution rate followed the same curve when the plate input power was raised to 2.0 w and the target temperature was 700°C.

Evolution of Strontium from SrO

The rates of evolution of strontium were studied using the radioactive tracer technique. For this investigation the getter was operated continuously to remove all gas evolved. The periods of bombardment required in studying the strontium evolution were much longer than required for the oxygen case because of the lower sensitivity of the method used for the detection of the strontium evolution. In the case of the evolution of oxygen, it was found that for bombardment at 25 v and 5 ma (current density of 25 ma/cm² at the target), the rate of evolution of oxygen was approximately 1.3×10^{10} atoms per cm² per sec. The surface density of oxygen or strontium ions in SrO is approximately 8×10^{14} ions/cm², and a sample of SrO 100 A thick contains approximately 40 layers of SrO. The removal of 10^{11} oxygen molecules (only 0.025% of the number of oxygen ions in a monolayer covering 1 cm² of surface) results in an increase in the gas pressure in a tube whose volume is 300 cc from 1×10^{-10} to 1×10^{-8} which can be detected to a high order of accuracy. In the case of the evolution of strontium, the activity of the Sr required counting times of the order of one hour to achieve a standard deviation of ±1%. Hence, if 10% of the strontium is removed, the probable error in the difference between the initial and final measurements of the target activity is ±10%. But 10% of 40 layers corresponds to 3.2×10^{15} ions whose removal requires a bombardment time of 2.5×10^5 seconds or approximately 60 hours. Hence, if practical periods of observation are to be used, the observations of the strontium evolution are of a considerably lower order of accuracy than the observations of the oxygen evolution.

In Fig. 6 the rate of evolution of strontium is compared to the rate of evolution of oxygen from the same target. The data above 60 v were taken keeping the target input power to 0.30 w, and the evolution rate was subsequently corrected to a constant input current of 5 ma. The two points for the rate of evolution of strontium at 200 v and 400 v are the maximum possible evolution rates at the limit of the probable error, so that the actual rate probably fell somewhere between the two dotted lines, as indicated on the curve.

It can be seen that at low energies the rates of evolution for both constituents are in fairly good agreement. At higher energies, however, the rate of evolution for the metal is far less than for oxygen when the target is operating at low temperatures.

Table I shows the evolution rate of oxygen and strontium as a function of the bombarding current density and temperature of the target when it is bombarded at an energy of 200 ev. At this energy the rate of evolution of oxygen apparently follows the square of the current density, while the metal evolution apparently varies more rapidly suggesting that there is a very strong temperature dependence, possible exponential. At 25.0 ma/cm² the metal evolution is approximately 10% of the oxygen evolution rate, while at 50 ma/cm² the ratio has increased to 0.6. A similar test at 30-electron volts showed no such temperature effect, since the evolution rates varied as the square of the current density up to a temperature of 550°C. The metal evolution rate for this case was approximately 0.6 that of the oxygen. Although insufficient data were taken at elevated temperatures in the high bombardment energy range to show whether the strontium evolution at the highest temperature had saturated, it is possible that this may have been the case and that the factor of 0.6 is the result of errors in the calibration. The difference in the temperature dependence of the strontium evolution in the low- and high-energy ranges strengthens the hypothesis that two different processes are involved for these ranges.

Evolution of Oxygen from BaO and MgO

The rates of evolution of oxygen from BaO and MgO were measured in the same manner as from SrO. The data from BaO and MgO are compared in Fig. 7 with those from SrO. Again the data above 60 volts were taken keeping the target power input to 0.3 watt and correcting the data to a constant current input of 5 ma after the current dependence was established. It will be observed that the general character of all the curves is the same, showing high- and low-energy processes. The efficiency for the process at higher energies for MgO appears to be a factor of 50 greater than for BaO and a factor of 5 greater than for SrO. The first thresholds for BaO and MgO are approximately 10 v and 18 v, respectively.

Figures 8 and 9 show the oxygen evolution rate as a function of the bombarding current density for BaO and MgO. The rates of evolution are also proportional to the square of the current density.

Contact potential differences between the target and the cathode were determined by the method devised by Lange[15] for triodes which is applicable here. The results are shown in Table II in which are listed the contact potential differences between the oxide-coated cathode serving as an electron source and the indicated electrode. In column 1 are given the target coatings; in column 2, the measured contact potential, V_p, between the cathode and the target; and in column 3, the measured contact potential, V_g, between the cathode and the control grid.

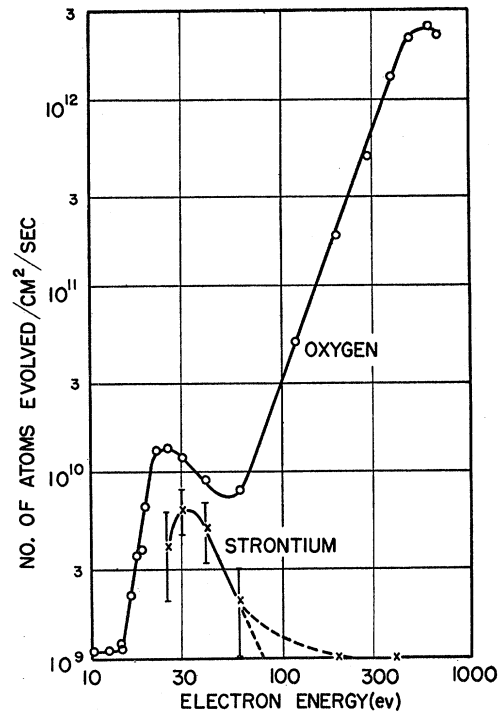[15] H. Lange, Z. Hochfrequenz. 31, 105–109 and 133–140 (1928).

FIG. 6. The evolution of oxygen and strontium from a SrO film as a function of the energy of the bombarding electrons at a current density of 25 ma/cm².

The grid wires in these tubes consisted of gold-plated tungsten. The accepted value for the work function for a well-activated oxide-coated cathode[16] is 1.0-electron
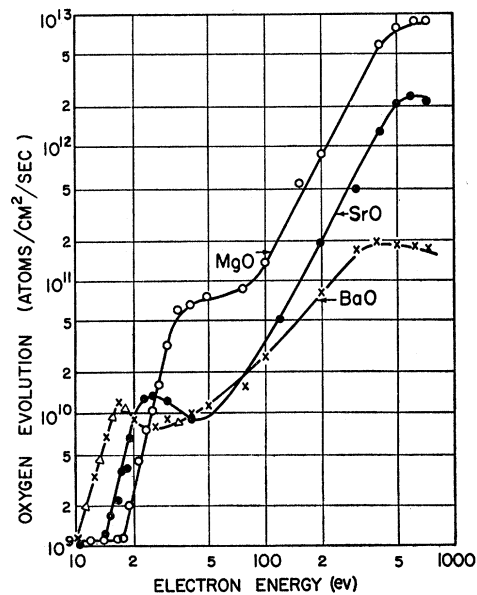

FIG. 7. The evolution of oxygen from films of SrO, MgO, and BaO as a function of the energy of bombarding electrons at a current density of 25 ma/cm².

[16] G. Herrmann and S. Wagener, The Oxide Coated Cathode (Chapman and Hall Ltd., London, 1951), Vol. II, p. 181.
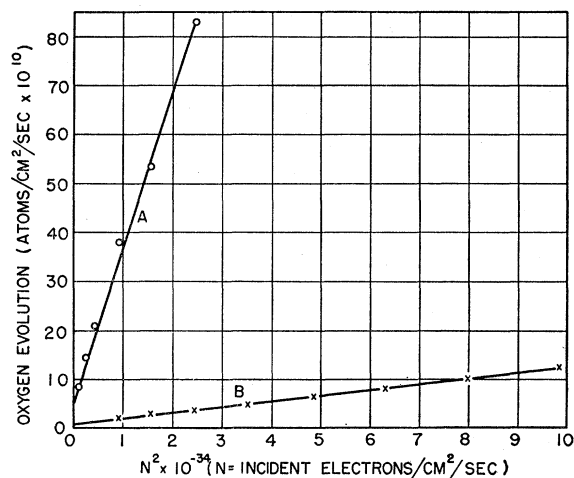
FIG. 8. Oxygen evolution as a function of the square of the number of electrons incident per cm² per sec on a BaO film. The energy of the incident electrons is, for curve A, 200 ev; and for curve B, 16 ev.

volt, while that for gold[17] is 4.8-electron volts. The difference of -3.8 ± 0.2 obtained from the data indicates the accuracy of the method.

DISCUSSION

Method

It will be realized that the technique employed for this study does not distinguish whether the oxygen and metal leave the surface as ions, atoms, or molecules. Since the oxygen was accumulated before measurement, it would be expected to be in molecular form at the time of measurement. The off-anode gradient during electron bombardment would be such as to prevent negative ions from leaving so that it is probable that the oxygen left in neutral form.

Energy Threshold for Dissociation and Efficiency

Without a physical understanding of the mechanism for the dissociation of oxides under electron bombardment it is not clear how the data should be extrapolated to determine a threshold energy for dissociation. However, since the evolution rate drops very rapidly in the neighborhood of the threshold, an apparent threshold may be obtained by graphical means.

The threshold was determined by noting the intersection of a straight line drawn through the the "background" evolution rate and a straight line through the initial six or seven points of the evolution curve on a log log plot. The results for BaO, SrO, and MgO are tabulated in Table III along with the values corrected for contact potentials and other pertinent data.

In dissociation phenomena, the efficiency of the process is of interest. In the present case the efficiency

[17] Reference 16, p. 98.

will depend on both the energy and the current density. From Figs. 5, 8, and 9 it can be seen that the evolution rate, Q, as a function of N, the number of incident electrons per cm² per sec, can be described by an equation of the form:

$$Q=\alpha N^2+C, \tag{1}$$

where α, a function of the bombarding energy, is the slope of the curve, and the constant C is the background evolution rate.

Mechanism for Dissociation under Electron Bombardment

In proposing a possible mechanism for the dissociation phenomenon we shall consider first the data obtained for low bombarding energies. Since the oxygen evolved depends on the square of the bombarding current density, the dissociation process appears to require two successive electronic excitations, as may be deduced from the following reasoning. The probability per unit time for the excitation by electron bombardment of a particular particle on the surface of a solid is given by

$$p(\epsilon) \propto j\sigma/e, \tag{2}$$

where j is the current density, σ is the cross section for the interaction, and e is the electronic charge. If two independent events are required:

$$p(\epsilon_1,\epsilon_2)=p_1p_2=kj^2\sigma_1\sigma_2/e^2, \tag{3}$$

where the subscripts 1 and 2 refer to the two excitations of the same particle required to produce the event. That two excitations are required to dissociate the alkaline earth oxides is not unreasonable in view of their divalent ionic character[18] if the dissociation produces neutral atoms.

The process proposed is as follows. At low energies, the electron penetration depth is very small, and it can be considered that the dissociation reaction takes place principally at the surface of the solid. It is proposed that dissociation may occur if both electrons on an oxygen ion are removed and placed on a neighboring strontium ion. In this way two neutral atoms are produced which may then escape. To show that such a surface effect is within the realm of possibility, we present the argument below.[19]

Consider a solid that contains n surface ions per cm². Under electron bombardment one eventually reaches an

TABLE II. Contact potential difference.

Target	V_p (volts)	V_g (volts)
SrO	0 ± 0.2	-3.8 ± 0.2
BaO	-0.5 ± 0.2	-3.8 ± 0.2
MgO	-1.1 ± 0.2	-3.8 ± 0.2

[18] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 81.
[19] We are indebted to Dr. A. J. Dekker for this suggestion.

equilibrium condition in which there are n_1 ions in the first excited state. Then, we may write

$$dn_1/dt = (n-n_1)N\sigma_1 - n_1 N\sigma_2 - (N_1/\tau) = 0. \quad (4)$$

The first term on the right represents the rate of production of ions in the first excited state, where N is the number of incident electrons per cm² per sec and σ_1 is the cross section for the first excitation. The second term represents the number of ions lost per second because of the second excitation, and the third term is the loss of ions due to the finite lifetime, τ, of the first excited state. From (4) we obtain

$$n_1 = \frac{nN\sigma_1}{N(\sigma_1+\sigma_2)+(1/\tau)}. \quad (5)$$

The rate of evolution of the atoms per cm² per sec is given by

$$Q = n_1 N \sigma_2, \quad (6)$$

whence

$$Q = \frac{nN^2\sigma_1\sigma_2}{N(\sigma_1+\sigma_2)+(1/\tau)}. \quad (7)$$

By (7) we see that a dependence on the square of the current density will occur if

$$N(\sigma_1+\sigma_2) \ll 1/\tau. \quad (8)$$

One may take as maximum values for the cross sections σ_1 and σ_2 the cross-sectional area of an oxygen ion which is of the order of 6×10^{-16} cm² and use for the lifetime, τ, the value of 10^{-8} sec normally assumed for the optical lifetime of an exciton.[20] For a bombarding current density of 25 ma per cm² or 1.6×10^{17} electrons per cm² per sec,

$$N(\sigma_1+\sigma_2) \simeq 2.5\times10^2,$$

and it is seen that condition (8) is easily met in the experiment. Hence (7) may be very accurately written:

$$Q = nN^2\sigma_1\sigma_2\tau. \quad (9)$$

Comparison of (9) with (1) shows that

$$\sigma_1\sigma_2 = \alpha/n\tau. \quad (10)$$

TABLE III. Observed energy thresholds for dissociation, thresholds corrected for contact potentials, and other pertinent data.

Oxide	Observed threshold ev	Corrected threshold ev	Forbidden band gap ev	Heat of[d] formation ev/molecule	Lattice[e] constant A
BaO	10.0±0.3	9.5±0.5	4.4[a]	5.78	5.50
SrO	14.0±0.3	14.0±0.5	5.6[b]	6.12	5.10
MgO	18.0±0.5	16.9±0.5	10.0[c]	6.34	4.20

[a] E. B. Hensley, University of Missouri (private communication to be published).
[b] R. L. Sproull, Phys. Rev. 78, 630 (1950).
[c] J. R. Nelson, Phys. Rev. 99, 1902 (1955).
[d] O. Kubachewski, and E. Evans, Metallurgical Thermochemistry (Butterworth-Springer, Ltd., London, 1951).
[e] Handbook of Chemistry and Physics (Chemical Rubber Publishing Company, Cleveland, 1949), thirty-first edition.
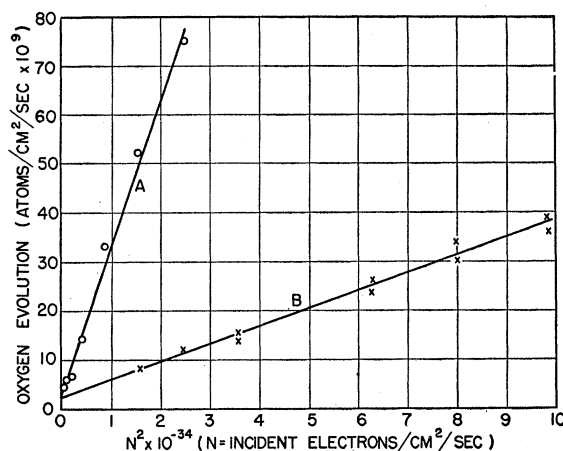
[20] F. Seitz, Revs. Modern Phys. 26, 29 (1954).

FIG. 9. Oxygen evolution as a function of the square of the number of electrons incident per cm² per sec on a MgO film. The energy of the incident electrons is, for curve A, 200 ev; and for curve B, 30 ev.

Equation (10) can be used in conjunction with the experimental data to determine the value for the product of the cross sections for the two excitations. The numerical value of α for 25-volt electrons bombarding SrO is 4×10^{-25}/cm²/sec, while the number n of surface oxygen ions per cm² is 8×10^{14}. Taking $\tau = 10^{-8}$ sec, we have

$$\sigma_1\sigma_2 = 5\times10^{-32} \text{ cm}^4, \quad (10b)$$

a result which appears reasonable in terms of atomic dimensions.

In the case of the process which becomes predominant in the higher energy range, a more complex situation exists. An important point to be kept in mind is that in this case the Sr is not liberated unless the surface is heated, in contrast to the case for the lower energy process. The depth of penetration of the primaries varies approximately as the square of the electron energy, so that excitations will occur at a rapidly increasing depth. Excitons so produced are very mobile and can rapidly diffuse through the oxide.[20] These excitons, if they arrived at the external surface, could cooperate together or with a direct electron interaction to produce dissociation. Presumably such a process should be essentially similar to the surface reaction postulated earlier with the rapidly rising efficiency resulting from the increasing production of excitons. However, the fact that the Sr does not evolve indicates that the situation is not so simple. If the process occurs principally on internal surfaces, the effects can be given a qualitative explanation. Oxygen released in this way would be expected to migrate through pores by Knudsen flow to the surface. However, since the vapor pressure of Sr at 300°C is low (10^{-7} mm Hg) it is likely that the Sr would condense in the pores and be liberated only when the temperature was increased. This explanation implies that the effec-

tive internal surfaces are much greater than the external surface.

The effect cannot be explained by proposing that the dissociation takes place in the bulk material and that the dissociation products subsequently diffuse to the surface or to pores, since very low diffusion coefficients have been found for both oxygen and the metal in these substances (even at high temperatures) by Sproull, Bever, and Libowitz[21] and Haxby.[22] The coefficients are too low to account for the rate of evolution of oxygen, and furthermore, if diffusion were the controlling mechanism, the oxygen evolution should have been strongly temperature dependent.

Until more experimental information on the process occurring at higher energies is available, additional speculation seems unprofitable.

It can be seen from Table III that one cannot directly connect the threshold energy for dissociation with the heat of formation or with the forbidden-band gap energy. The energy required to produce an exciton is somewhat less than the forbidden-band gap energy, so that the threshold energy would not correspond to the exciton energy either. It is possible, however, that when an exciton is produced, the remaining electron on the oxygen may be bound somewhat more strongly, and in consequence the threshold energy would be determined by the energy required to excite the remaining electron to a strontium ion.

Comparison of the Results with the Literature

Quantitative results for the rates of evolution of dissociation products as a function of the bombarding electron energy or current density, in general, cannot be found in the literature. In 1954, Yoshida et al.[7] reported results in which they bombarded SrO containing Sr^{89} and detected the evolution of Sr by the radioactive tracer technique. They noticed that the evolution of Sr increased exponentially with the target temperature when it was bombarded with 150-volt electrons. They also observed that at a target temperature of 450°C the strontium evolution was smaller when the oxide was bombarded with 500-volt electrons than was the case for bombardment with 150-volt electrons. Although they tabulated the bombarding currents, they did not provide data which would permit calculation of the current densities, so that a direct comparison of their results cannot be made with those in this work. However, it can be seen that both sets of results are in qualitative agreement.

More recently these same authors[23] have studied the dissociation of BaO under electron bombardment. They report that the Ba evolved from a target bombarded by electrons of 150-ev energy increases exponentially with

the temperature over the range 600 to 710°K. They further reported a linear dependence on current for the rate of evolution of Ba and an exponentially decreasing dependence of the rate on the square root of the bombarding voltage, in the range 90 to 500 v. Their linear dependence of the evolution with current is in direct disagreement with the results reported here. Their data were obtained for bombarding voltages which would correspond to the range of the higher energy process for BaO if one is justified in assuming that processes for BaO and SrO are alike. Since the metallic evolution of Ba was not observed in our case, no direct comparisons are warranted, but the exponential dependence of the barium evolution on temperature would be consistent with our observations on strontium. The exponentially decreasing evolution of barium as a function of the square root of voltage is in disagreement with our findings for the oxygen evolution from BaO over the same energy range and would require postulating different mechanisms for the release of Ba and O.

Others who have investigated the problem, such as Jacobs, Metson, Wright, and Woods, and Amakasu, previously mentioned, did not show quantitative results, but measured only the threshold energy for dissociation using the cathode poisoning method. In general, the results in this work are in disagreement with these observers. Jacobs and Metson found that the threshold was equal to the heat of formation, while in this work no apparent correlation has been found, as can be seen from Table III. Wright and Woods and Amakasu also found no correlation with the heat of formation, but observed a threshold of 4 ev for BaO. This value is in disagreement with the 9.5-ev dissociation energy found here.

Since these observers could not make quantitative measurement and were not able to identify positively the dissociation products, it is felt that their results were subject to misinterpretation. Metson, for example, found a threshold of 5.56 ev which he attributed to BaO, and a second threshold of 9.4 ev on the same target which he attributed to $BaCl_2$ or $BaSO_4$ which may have evaporated from the cathode. In the work reported here it is observed that adsorbed gas was released in the vicinity of 5 ev and that true dissociation occurred at 9.5 ev. Consequently, it is possible that Metson's lower threshold was due to adsorbed gas and the higher value was due to dissociation of BaO, in which case the two results would be in agreement.

CONCLUSIONS

Oxygen is released from BaO, SrO, and MgO when thin films of these materials are subjected to electron bombardment at energies above 9.5 ± 0.5, 14.0 ± 0.5, and 16.9 ± 0.5 ev, respectively. The proportionality between the rate of oxygen evolution and the square of the current density indicates that a two-step electronic excitation of the solid is required for dissociation.

[21] Sproull, Bever, and Libowitz, Phys. Rev. 92, 77 (1953).
[22] B. V. Haxby, Phys. Rev. 99, 1636 (1955).
[23] Yoshida, Shibata, Igarashi, and Arata, J. Appl. Phys. 27, 497 (1956).

In the case of SrO the temperature dependence of the evolution of Sr suggests that the dissociation at low energies is a surface reaction while at high energies a reaction within the solid occurs. Additional support for this suggestion is provided by the variation of the oxygen evolution with the energy of the incident electrons. The release of oxygen from materials bombarded with electrons having energies near 5-electron volts, which has frequently been ascribed to a dissociation process, appears rather to result from a desorption of a gas film.

Opto-Electronic Properties of Mercuric Iodide

RICHARD H. BUBE

RCA Laboratories, Radio Corporation of America, Princeton, New Jersey

(Received February 8, 1957)

The optical and photoelectrical properties of mercuric iodide crystals and layers have been investigated, particularly as affected by the phase transformation from tetragonal (low-temperature form) to orthorhombic (high-temperature form) which occurs at 400°K. The largest temperature coefficient for band-gap variation of any known material is found for the orthorhombic form: -24×10^{-4} ev/degree. The following phenomena are discussed: (1) location and temperature dependence of absorption edge by measurements of transmission, reflectivity, and photoconductivity response spectra; (2) temperature dependence of dark current; (3) electrode effects in photoconductivity; (4) variation of dark current and photocurrent through the phase transformation; (5) thermally-stimulated-currents; (6) variation of photocurrent with voltage, light intensity, and temperature. Temperature-quenching of photoconductivity in HgI_2 crystals can be described by means of the same analysis as has been applied to various $A^{II}B^{VI}$ photoconductors, giving a location of 0.5 ev above the valence band for the "sensitizing" centers in HgI_2.

1. INTRODUCTION

MERCURIC iodide was one of the earliest materials to be investigated for photoconductivity. In 1903, it was shown[1] that HgI_2 could be used with gelatin to form a photographic emulsion. Other workers studied the spectral response and the mechanism of photoconductivity.[2-4] Nix[5] reported that the photosensitivity of HgI_2 crystals grown from ethyl alcohol solution was lost after about a year, as the crystals became polycrystalline, but could be restored by the application of a field. Putseiko[6] studied photoconductivity and dye-sensitization phenomena in HgI_2. Chepur[7] discussed the formation of melted-and-recrystallized layers, crystals grown from the melt, and crystals grown from acetone solution, together with their photoconductivity. The existence of excitons in HgI_2 has been indicated by Nikitine[8] and by Gross[9]; Gross has also reported that the photosensitivity of the orthorhombic form of HgI_2 is about 0.1% of that of the tetragonal form. A study of the phase-transformation kinetics has been reported by Newkirk[10] for the transformation of the "red" tetragonal form of HgI_2 to the "yellow" orthorhombic form with increasing temperature at about 400°K; he has shown that the transformation consists of a shift of the (100) plane in the tetragonal form to the (110) plane in the orthorhombic form; the [001] direction is preserved.

The present investigation was motivated originally by interest in the effects of the phase transformation on the optical and photoelectrical properties of HgI_2. As the work progressed, however, this investigation was broadened to include many of the semiconducting and photoconducting characteristics of HgI_2: temperature dependence of the band-gap; low-temperature luminescence; electrode problems; temperature dependence of dark current; dependence of photocurrent on voltage, light intensity, temperature, and wavelength; and thermally stimulated currents.

2. MATERIAL PREPARATION

Samples of HgI_2 were measured (a) in microcrystalline (powder) form, (b) as sintered layers produced by vapor deposition, (c) as melted and recrystallized polycrystalline layers, (d) as crystals grown from the

[1] Luppo-Cramer, *Eder's Jahrbuch* (1903), p. 24.
[2] G. Athanasiu, Compt. rend. **176**, 1389 (1923).
[3] M. Volmer, Z. wiss. Phot. **16**, 152 (1916).
[4] F. Kampf, Physik. Z. **23**, 420 (1922).
[5] F. C. Nix. Phys. Rev. **47**, 72 (1935).
[6] E. K. Putseiko, Izvest. Akad. Nauk, S.S.S.R., Ser. Fiz. **16**, 34 (1952); E. K. Putseiko and A. N. Terenin, Doklady Akad. Nauk, S.S.S.R. **70**, 401 (1950).
[7] D. V. Chepur, Zhur. Tekh. Fiz. **25**, 2411 (1955).
[8] S. Nikitine, Compt. Rend. **240**, 1324 (1955).
[9] E. F. Gross, Zhur. Tekh. Fiz. **25**, 1661 (1955).

[10] J. B. Newkirk, Acta Metallurgica 4, 316 (1956).