

voltages; these effects are related to the release rate of the trapped electrons and to depletion of traps or centers or both.<sup>11</sup> The mechanism of ac-dc amplification depends very little, however, upon ac frequency as is to be expected from its nature. The evidence that the spectrum of the ac-dc emission is identical to that of the ac emission and somewhat different from the spectrum of the dc emission, also supports the assumption that the former are closely related and differ essentially from the dc emission. The difference, on the

basis of the theory presented here, is simply that the recombination-emission process in ac and ac-dc electroluminescence occurs in a low-field region of the phosphor crystal while dc emission occurs in crystal regions experiencing a high electric field.

#### ACKNOWLEDGMENTS

It is a pleasure to acknowledge the help of R. L. Fitzmaurice and to thank H. F. Ivey for helpful discussion and encouragement.

PHYSICAL REVIEW

VOLUME 113, NUMBER 5

MARCH 1, 1959

### Electroluminescence in Cuprous Oxide\*

R. FRERICHS AND R. HANDY  
Northwestern University, Evanston, Illinois  
(Received August 18, 1958)

This paper reports the observation of electroluminescence in cuprous oxide. The variations in electroluminescent light output have been studied as a function of excitation frequency, wave shape, voltage, current, and power as well as for changes in ambient temperature. These basic properties are presented in graphic form and show that  $\text{Cu}_2\text{O}$  does not fit readily into either of the two general classes of electroluminescent materials, but possesses new and unusual properties of its own.

The electroluminescence can be observed in cuprous oxide plate rectifiers and in point contact structures. In the plate rectifiers, changes in electrical properties known as current creep occur during excitation which are reflected in the light emission from the plates. This effect was studied in detail and a new theoretical model proposed that satisfactorily accounts for the observed changes in the electrical properties, as well as for the published observations on commercial  $\text{Cu}_2\text{O}$  rectifiers.

Unusual memory properties have been observed that permit the initial electroluminescent light output to be enhanced by prebiasing with direct currents. This phenomenon is traced to the movement of matter within the material during the biasing interval.

#### INTRODUCTION

**C**UPROUS oxide is a semiconductor and a phosphor. When illuminated with visible light it emits a predominant infrared band extending from 0.8 to 1.4 microns with the maximum emission peak occurring at about 0.95 micron.<sup>1,2</sup> The cathodoluminescence of  $\text{Cu}_2\text{O}$  was found by Frerichs and Weichman.<sup>3</sup> Their investigation showed that plates of cuprous oxide emit strongly in the infrared region when bombarded by electrons. It was a logical next step to place a transparent electrode on a plate, apply a field, and search for infrared electroluminescence with an image converter.

#### EXPERIMENTAL PROCEDURES

Polycrystalline plates of  $\text{Cu}_2\text{O}$ -covered copper and of pure  $\text{Cu}_2\text{O}$  prepared by Weichman were used.<sup>3,4</sup> Two

emitting structures were found. First a sandwich arrangement with a  $\text{Cu}_2\text{O}$ -covered copper plate clamped against a transparent NESAs electrode, and second a pure piece of  $\text{Cu}_2\text{O}$  (transparent) with an evaporated gold electrode and one or more point contacts (now under study). The reported observations were made with a sandwich cell, Fig. 1, sealed in a vacuum flask, Fig. 2, which contained provisions for cooling or heating the sample. The vacuum chamber prevented frost formation during low-temperature experiments and eliminated uncontrolled surface contamination. The emission

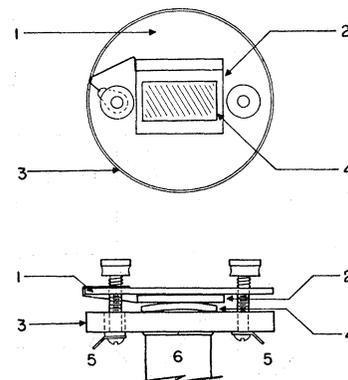


FIG. 1. Electroluminescent cuprous oxide cell: (1) glass cover plate, (2) NESAs glass, (3) copper block, (4)  $\text{Cu}_2\text{O}$  covered plate, (5) electrical contacts, (6) Kovar cylinder.

\* This paper represents a part of the thesis for the Master of Science degree in the field of Electrical Engineering by R. M. Handy. A short report on this work was given by R. Frerichs and R. M. Handy at the Washington Meeting of the American Physical Society, May, 1958 [Bull. Am. Phys. Soc. Ser. II, 3, 219 (1958)].

<sup>1</sup> M. Seibt, *Verhandl. deut. physik Ges.* **20**, No. 2, 99 (1939).

<sup>2</sup> V. E. Lashkarew and A. M. Kossonogowa, *Compt. rend. acad. sci. U.R.S.S.* **54**, 124 (1946).

<sup>3</sup> R. Frerichs and F. Weichman, *J. Appl. Phys.* **29**, 710 (1958).

<sup>4</sup> F. Weichman, Ph.D. thesis, Physics Department, Northwestern University, 1958 (unpublished), containing the detailed description of the method used.

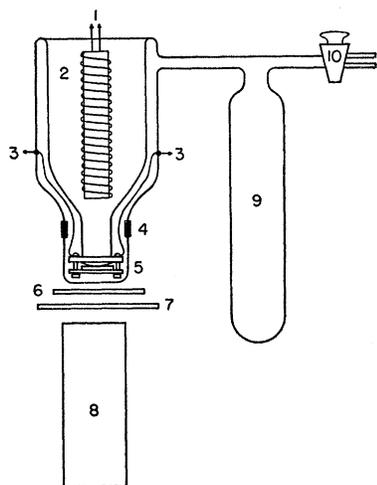


FIG. 2. Vacuum chamber: (1) heater leads, (2) Dewar flask, (3) electrical contacts for cell, (4) ground joint, (5) electro luminescent cell, (6) shutter, (7) filter, (8) photomultiplier tube, (9) charcoal trap, (10) stopcock.

was detected by use of an image converter and a Dumont K 1292 infrared sensitive photomultiplier tube. Both were equipped with infrared filters opaque up to 0.76 micron. The emission from the electro luminescent sandwich is small compared with the background radiation of a lighted room; therefore the vacuum apparatus and photomultiplier tube were enclosed in a light-tight box.

Provisions were made for filling or emptying the temperature bath, replenishing the liquid air supply to the vacuum charcoal trap, operating the opaque shutter, and making connections to the power supplies and measuring systems without removing the cover.

The electro luminescence in  $\text{Cu}_2\text{O}$  can be observed continuously with dc or ac excitation. The dc supply was obtained from batteries and the ac of various frequencies was obtained from an oscillator-amplifier combination with an external feedback loop to provide voltage stabilization. Most ac measurements were made using 200 cps as a convenient value. Rapid changes in photomultiplier output were observed on a Tektronix Model 545 Dual Channel cathode-ray oscilloscope. Slow changes in average output were observed by use of a dual-channel Sanborn pen recorder. The pen recorder does not respond above 70 cps so input-output comparisons for ac excitation were made using rectifiers and filters at the recorder input to obtain a trace proportional to the average signal.

The durability of the cell is excellent. A single cell has

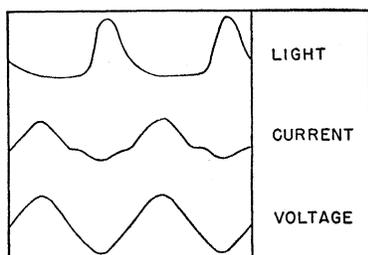


FIG. 3. Light and current wave forms for 200-cps sinusoidal input voltage.

been in operation for over six months without loss of electro luminescent properties. Voltages of 0-400 volts were used without apparent damage to the cell. For a deliberate failure test over 900 volts rms 60 cps ac were required to destroy a plate. The voltage tolerance of the cell is much higher than that usually found with commercial  $\text{Cu}_2\text{O}$  rectifiers because of the heavy (0.5 mm) oxide layers used.

This heavy layer of oxide presents a large bulk resistance in series with the thin barrier region and reduces the over-all rectification ratio of the cell to about 2:1.

#### WAVE FORM OF EMITTED LIGHT

Figure 3 illustrates the light wave form produced by 200-cps sinusoidal excitation. The current curve shows the rectifying properties of the cell. Light is emitted only during the reverse conduction phase, (i.e., Cu positive,  $\text{Cu}_2\text{O}$  negative) and pulses at the same rate as the applied frequency. The emission of light is coincident with the occurrence of high fields in the barrier region of the rectifier, since under reverse conduction a substantial portion of the applied voltage will be concentrated across the thin barrier region at the Cu-Cu<sub>2</sub>O interface. The light response to square pulses is shown

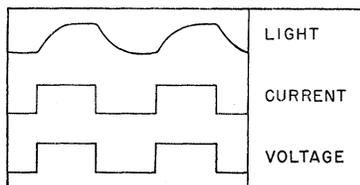


FIG. 4. Light and current wave form for 4-msec voltage pulse (reverse conduction direction).

in Fig. 4. 100-volt pulses of 4-msec duration were applied in the reverse direction. The rise and decay half-times of emission are observed to be about 1 msec. This predicts a drop in average light emission as excitation frequency increases, as was subsequently observed.

#### VARIATIONS IN OUTPUT

Studies of brightness *versus* excitation are complicated by slow but reversible changes in cell properties due to (a) loss of emission efficiency with time, and (b) current creep.<sup>5</sup> Figures 5 and 6 illustrate the results of continuous ac and dc excitation, respectively. They were made by recording average light emission and average *reverse* current with the Sanborn pen recorder for *constant* applied voltage. The input filter on the recorder prevents the individual light or ac current pulses from being resolved and the small fluctuations in the light trace represent low-frequency noise. The light emission in Fig. 5 drops to a quiescent value within a few seconds after application of the ac excitation. Since the applied voltage was constant during this interval, the change in output may be interpreted as a decrease in emitting

<sup>5</sup> See H. K. Henisch, *Metal Rectifiers* (Clarendon Press, Oxford, 1957), p. 113 ff.

efficiency. A similar effect is observed for the light trace of Fig. 6 except that a stable value is not reached until several minutes have elapsed. In both cases interruption of the excitation results in a partial recovery of emission efficiency, and on reapplication the output again drops toward a quiescent value. The way in which recovery depends upon the duration of the interruption will be treated in a later paragraph under memory effects.

The average ac current curve in Fig. 5 showed little change during the excitation interval. The dc current curve of Fig. 6, however, increased steadily under constant voltage. This is positive current creep. Current creep is a well-known but little understood phenomenon of plate rectifiers and manifests itself as an increase (positive creep) or decrease (negative creep) in current through the rectifier with time under constant voltage. From Fig. 6 it is apparent that current creep will have a pronounced effect on any brightness *versus* excitation measurements; therefore a detailed study of creep phenomena is required.

FIG. 5. Changes in emission with ac excitation.

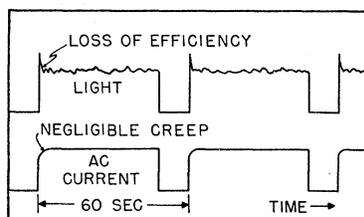
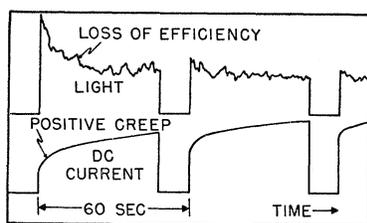


FIG. 6. Changes in emission with dc excitation.

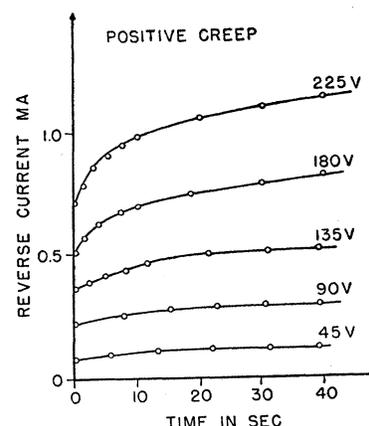


#### CURRENT CREEP

The rate and magnitude of creep depends upon the applied voltage as shown in Figs. 7 and 8. Positive creep is produced by reverse voltage and negative creep by forward voltage. It should be noted that for equal magnitude of voltage and equal time, the amount of creep produced is nearly equal but of opposite sign. It is noted in Fig. 6 that interruption of the applied dc voltage for a short period alters the rate of change of current and a new creep curve results. If the voltage is removed and the cell is allowed to rest, the effects of creep will slowly decay ("uncreeping") and the original properties of the cell will be recovered. This process may take several hours or days, however, depending upon the initial amount of creep.

There are several other important properties associated with current creep. First, while creep changes the total current through the cell it does not markedly

FIG. 7. Positive creep resulting from various applied voltages.

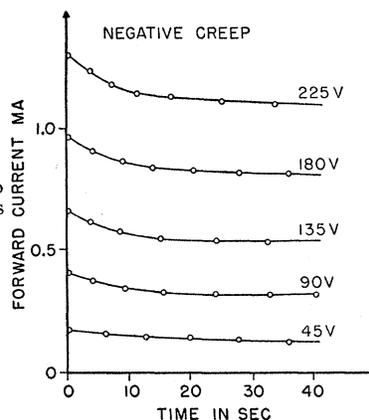


change the rectification ratio. Second, if the cell has been allowed to rest until "uncreeping" is substantially complete, then forward voltage will not produce creep. *This means that in order to observe negative creep the cell must have undergone positive creep in the recent past either from reverse dc voltage or from prolonged application of ac voltage.* It can be concluded that when forward voltage produces negative creep it is accomplishing the same return to the original properties of the cell as would be produced by prolonged rest, but at an accelerated rate.

#### BRIGHTNESS CHARACTERISTICS

The effect of current creep is to alter the electrical properties of the cell during test, and to make its electrical properties at any instant depend to some extent on all previous tests. Determination of the brightness characteristics thus requires a test procedure which cancels out creep effects. It was found that short pulses (80 msec) of alternating polarity separated by a relatively long time interval (4 to 6 sec) produced results independent of creep and untroubled by changes in emission efficiency. Whenever possible this technique was used for all brightness measurements since it produces consistent results relating the initial brightness

FIG. 8. Negative creep resulting from various applied voltages.



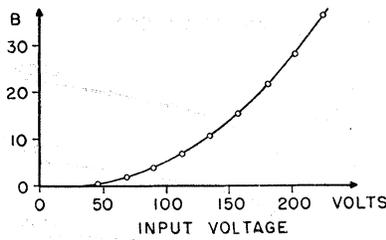


FIG. 9. Initial brightness *versus* input reverse voltage.

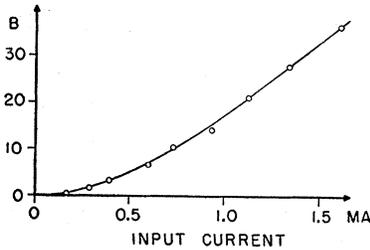


FIG. 10. Initial brightness *versus* input reverse current.

to input voltage, current, and power. Throughout this paper, brightness  $B$  and change in brightness  $\Delta B$  are given in arbitrary units.

Figures 9, 10, and 11 show the initial emission as a function of input voltage, reverse current, and reverse power. Only the input in the reverse direction is considered since forward conduction does not produce light. The most significant result obtained is the *linear dependence of initial emission upon the reverse power input.*

#### TEMPERATURE DEPENDENCE

Emitted light intensity was found to change with temperature. The exact form of this change was measured between  $-60$  and  $+50$  degrees centigrade. A rapid change in electrical properties also occurs as temperature varies. Alternate pulse techniques were again used to avoid altering cell properties during measurement. The change in emission for a constant power input of 100 mws is shown by Fig. 12. A broad maximum is seen to occur near zero degrees centigrade. The efficiency is greatest in this region, dropping off as temperature rises or falls.

#### BIASED EMISSION CHARACTERISTICS

So far the effects of current creep have been deliberately avoided in making quantitative measurements.

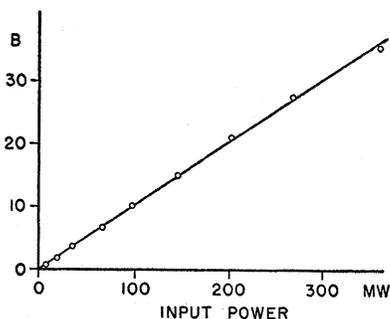


FIG. 11. Initial brightness *versus* input reverse power.

It is possible to make use of these effects to enhance the initial emission from the cell. Earlier in this section it was demonstrated that continuous dc excitation could produce large creep effects, but that ac excitation produced only a small amount of creep. In fact, ac excitation following a period of large dc creep will permit "uncreeping" to progress largely without interference. Figures 13 and 14 show effects of "prebiasing" the cuprous oxide cell by connecting it first to the battery and then switching it to ac excitation.

The upper trace in each figure represents the average light output, the middle trace the average ac current level, and the lower trace the dc biasing current. The time scale increases from left to right. At first the ac is applied for about 50 sec, removed for 10 seconds, and then reapplied. During the subsequent removal, however, a constant dc biasing voltage is applied. In Fig. 13 the dc is applied in the direction tending to produce light. The positive current creep is readily observable from the increase in dc bias current over the 10 second interval. At the end of this 10 sec the dc is removed and the ac signal again applied. There is an immediate increase in the light output from the plate that decays

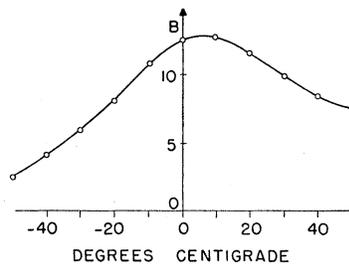


FIG. 12. Initial brightness as a function of temperature for constant power input.

slowly over the ensuing 50 sec. If the sequence is repeated the same phenomenon occurs again.

In Fig. 14 the same procedure is followed except that the dc potential is changed to correspond to the non-light producing direction of current flow, the forward direction. Negative current creep is observed. More important, however, is the effect upon the light output. A larger momentary enhancement is obtained but its decay is very rapid by comparison, all but disappearing in less than two seconds.

In both cases the change in electrical properties produced by dc current creep resulted in a change in ac current levels through the cell that gradually disappeared. Thus, some "uncreeping" progressed even under ac excitation.

The enhancement of initial light emission was found to stem from two causes: (a) the natural recovery of emission efficiency that occurred during the biasing interval, and (b) the effects of the biasing current. These effects can be separated by measuring the increase in initial emission as a function of unbiased delay time, and then as a function of biasing time for different biasing voltages. The results are presented in Figs. 15 and 16 showing the enhancement of the initial light

burst above the quiescent level as a function of time. It can be seen that the biasing currents are very effective in enhancing the initial light level, and that the degree of enhancement depends not only on the duration and magnitude of the bias, but on the direction as well. Reverse bias requires nearly twice the bias time to produce the same degree of initial enhancement.

If enhancement by reverse biasing requires longer bias times for the same effect, then it is reasonable to expect that the decay of this enhancement would in turn take longer. Such a fact was demonstrated by Fig. 13, but is more clearly shown by comparison of the total enhancement decay time presented in Figs. 17 and 18. The total decay time for reverse biasing is observed to be approximately twice as great as that for forward biasing of equal voltage and equal bias time. It is also noted that only a very slight increase in total decay time occurs due to natural recovery of emission efficiency by unbiased delay. It is clear then that biasing

FIG. 13. Light enhancement by pre-biasing with reverse dc voltage.

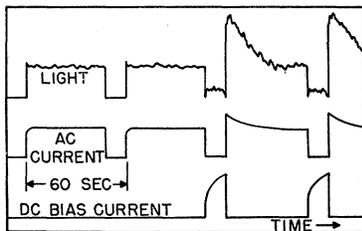
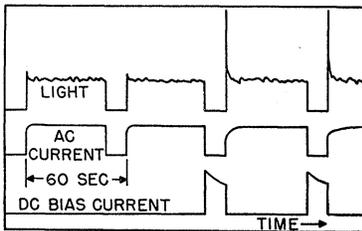


FIG. 14. Light enhancement by pre-biasing with forward dc voltage.



the cell with direct signals prior to application of the ac produces substantial changes in the total decay time of initial emission. Furthermore, it is clear that reverse biasing takes roughly twice as long to produce the same initial effect, and the effects last roughly twice as long.

The observed difference between forward and reverse bias decay times are more dramatically shown if the half-time of decay (Fig. 19) is considered rather than the total time (Figs. 17 and 18). For forward bias the greatest half-time of decay observed was approximately one second, for a total decay time of 120 sec, and total bias time of 231 sec. Clearly then all but a small fraction of the enhancement disappears in less than 2 sec. By contrast the greatest half-time of decay observed for reverse bias was approximately 37 sec for a total decay time of 274 sec, and a bias time of 206 sec. It is seen then that while the total decay time may be only twice as great, the half-time of decay can be between 30 and 40 times as great. The initial enhancement produced by

FIG. 15. Enhancement of initial light emission as a function of bias time for several reverse bias voltages.

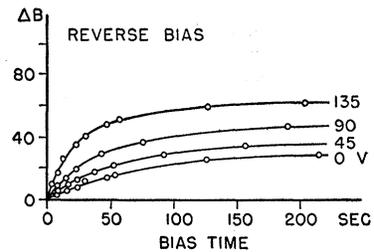
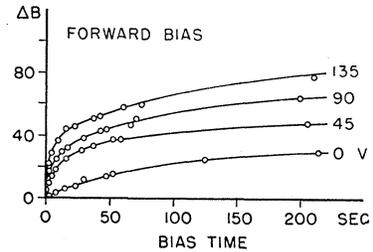


FIG. 16. Enhancement of initial light emission as a function of bias time for several forward bias voltages.



reverse bias not only lasts longer, but also decays at a much different rate than that produced by forward bias. The cell thus *remembers* the effects of reverse bias in a much different way than it does the effects of forward bias.

Another question must be answered. How long does the memory of the prebiasing treatment persist in the cell, and how does it change with time? This can be ascertained by delaying the application of the ac signal after a fixed biasing interval is completed. Changes in the enhancement of the initial light level then can be measured as a function of the delay time. A saddle-shaped curve is obtained as shown by Figs. 20 and 21. It results from the cumulative effects of loss of memory as delay time increases and from natural recovery of higher efficiency due to the elapsed rest (delay) time. Since the rate of natural recovery may be measured independently, the two effects may be separated as

FIG. 17. Total enhancement decay time is a function of bias time for several reverse bias voltages.

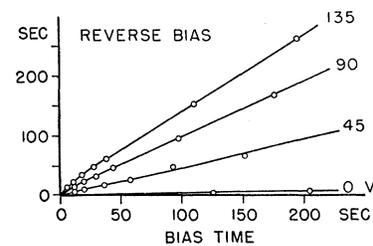
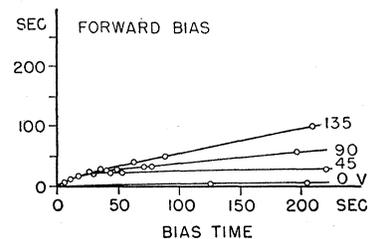


FIG. 18. Total enhancement decay time as a function of bias time for several forward bias voltages.



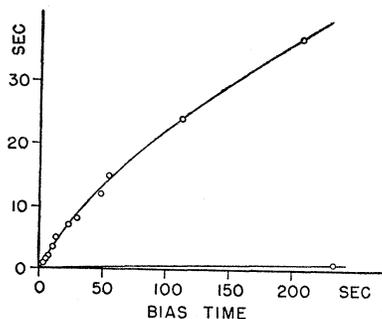


FIG. 19. Half-time of enhancement decay time as a function of bias time: Upper curve, reverse bias, lower curve, forward bias.

shown by the dotted lines. The rate of memory loss is clearly seen.

#### EFFECTS OF BIASING ON THE PHASE OF LIGHT EMISSION

Investigation of reverse bias enhancement effects with a cathode-ray oscilloscope<sup>6</sup> showed that the curves of Fig. 13 result from the superposition of two trains of light pulses, corresponding to the forward and reverse phases of current flow. Forward current produces a decreasing series of pulses and reverse current produces an increasing series, Fig. 22. Within a short time the forward phase pulses have disappeared while the reverse phase pulses reach the quiescent level characteristic of the voltage applied to the cell. Forward bias enhancement results only from a series of decreasing pulses corresponding to the reverse phase of the ac excitation. No forward phase pulses are produced.

#### BASIC ELECTRICAL PROPERTIES

Cuprous oxide is known to be a *p*-type semiconductor with conductivities ranging from  $10^{-2}$  to  $10^{-10}$  per ohm-cm.<sup>5,7,8</sup> Acceptor centers are created by copper atom vacancies in the lattice. These vacancies become ionized by capturing an electron from a nearby

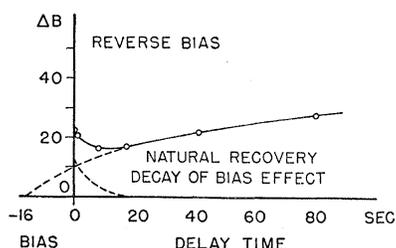


FIG. 20. Enhancement of initial light emission as a function of delay time following a 16-sec reverse biasing interval.

<sup>6</sup> From data obtained by I. Liberman, Department of Electrical Engineering, The Technological Institute, Northwestern University, Evanston, Illinois.

<sup>7</sup> G. W. Castellan and W. J. Moore, *J. Chem. Phys.* **17**, 41 (1949).

<sup>8</sup> W. J. Moore and B. Selikson, *J. Chem. Phys.* **19**, 1539 (1951).

copper ion which thereby assumes a divalent state ( $\text{Cu}^+ - e^- \rightarrow \text{Cu}^{++}$ ). The divalent state is not firmly fixed to the individual copper ion and it constitutes a free hole which can migrate through the crystal by a continuous exchange of valence electrons between copper ions.

When a *p*-type semiconductor is brought into contact with a metal of lower work function, a rectifying junction will be formed.<sup>9</sup> A barrier layer is formed at the Cu-Cu<sub>2</sub>O interface which will be raised or lowered by the applied voltage as shown in Fig. 23. These changes in barrier height as seen from the semiconductor result in asymmetric conduction. It should be noted, however, that the barrier height as seen from the metal is not affected by the applied voltage.

#### THEORY OF CURRENT CREEP

The predominant creep mechanism is known to be positive creep, that is, the increase of *reverse* current with time for a constant applied voltage. If the reverse current is to increase with time, then a decrease in the height of thickness of the barrier ( $E_s - \phi_m$ ) as seen from

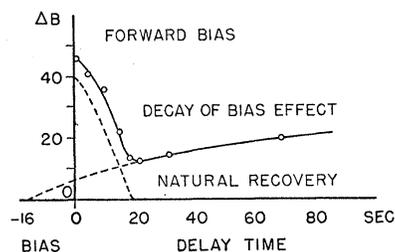


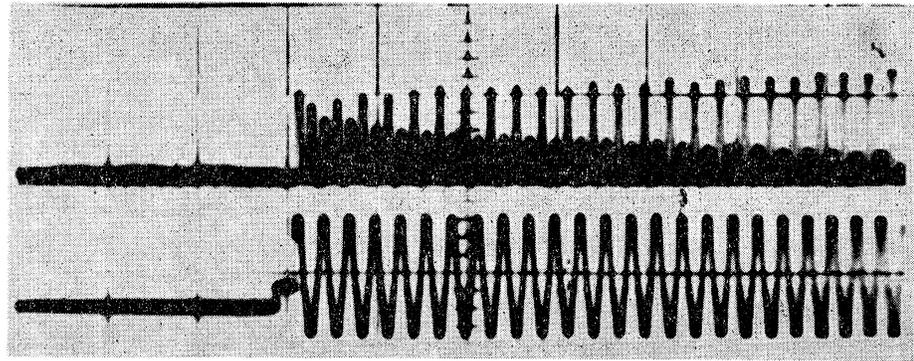
FIG. 21. Enhancement of initial light emission as a function of delay time following a 16-sec forward biasing interval.

the metal must slowly take place. This can occur only by changes within the barrier region, since changes in the bulk semiconductor or metal do not affect ( $E_s - \phi_m$ ). Rectifying barriers are formed by metal to semiconductor contacts only when the difference in the work function produces a space charge layer in the semiconductor. In *p*-type materials this space charge layer is due to ionized acceptors. The height and thickness of the barrier as seen from the metal is controlled by the number and distribution of ionized acceptors in the barrier region. If the acceptor concentration in the barrier region is slowly increased by the applied voltage, then the barrier will become narrower and more transparent and positive current creep will take place.

The relatively slow rate at which creep occurs rules out electronic processes as a basis for creep theory and leads to a theory based upon ionic migration. Henisch<sup>5</sup> reaches the same conclusion by analogy to selenium rectifiers requiring a forming process, but does not elaborate on the actual mechanism in Cu<sub>2</sub>O. The effect

<sup>9</sup> A. Van Der Ziel, *Solid State Physical Electronics* (Prentice-Hall, Englewood Cliffs, New Jersey, 1957), pg. 241 ff.

FIG. 22. Cathode ray oscilloscope curves of individual light pulses after reverse biasing. Upper traces are light pulses showing decreasing and increasing pulse trains. Lower trace is ac current with polarity as follows: forward phase upwards, reverse phase downwards.



of ionic migration can be briefly stated as follows. Figure 24 shows a schematic representation of this process. For a more complete treatment see Handy.<sup>10</sup>

(a) The acceptor concentration (copper atom vacancies) will drop sharply as one approaches the interface from the semiconductor and excess copper ions will be found.<sup>5</sup>

(b) Copper ions diffuse through solid  $\text{Cu}_2\text{O}$  by successively occupying vacant lattice sites.<sup>11</sup>

(c) Reverse voltage creates a high field in the barrier region which drives excess copper ions away from the interface, creating in their place additional copper ion vacancies (ionized acceptor centers).

(d) The acceptor center concentration in the barrier region is thus increased and those previously present may be moved sufficiently close to the metal interface to be neutralized by the surface charge on the metal. The height and width of the barrier region as seen from the metal is thus slowly decreased as migration progresses, permitting an increase in reverse current, and hence positive current creep.

(e) Migration continues until the excess copper ions move into a region of lower field. This process forms an

acceptor-center depletion layer i.e., a copper-rich region at the edge of the barrier region in the semiconductor.

(f) Migration of the excess copper ions and hence acceptor centers creates a concentration gradient  $AB$  (Fig. 24) which will cause the cell to recover its original properties when the field is removed.

(g) If the field on the cell is sufficiently strong or applied for extended periods, the acceptor depletion layer will be partially filled by continued migration of excess copper into the bulk of the semiconductor. If the field is then removed, the concentration gradient will be smaller and the original properties will not be recovered. This is recognized as the familiar aging phenomenon in  $\text{Cu}_2\text{O}$  plate rectifiers.

#### EMISSION PROPERTIES

Much work has been done on the luminescent properties of cuprous oxide.<sup>1-3,12,13</sup> An energy band model has been constructed<sup>12,13</sup> which correlates the emission spectrum with the existence of vacancies in the crystal lattice. Since both photoluminescence and electroluminescence include the same spectral region, it is concluded that the band model applies equally well to electroluminescent emission. The observed electro-

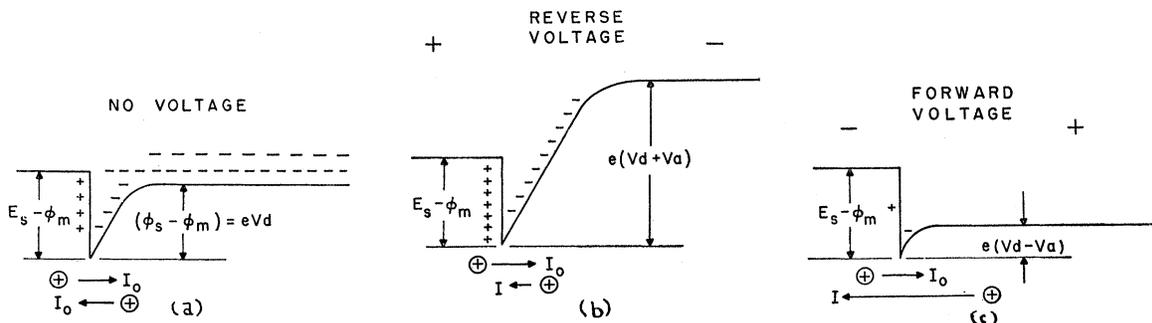


FIG. 23. Energy band model of  $p$ -type rectifying junction showing valence band only.  $\phi_s$ =work function of semiconductor,  $\phi_m$ =work function of metal,  $V_d$ =diffusion potential,  $V_a$ =applied voltage,  $E_s$ =depth of top of filled band below vacuum level,  $I_0$ =diffusion current. (a) No voltage, (b) reverse voltage applied, and (c) forward voltage applied.

<sup>10</sup> R. Handy, M.S. thesis, Electrical Engineering, Northwestern University, 1958 (unpublished).

<sup>11</sup> Bardeen, Brattain, and Shockley, J. Chem. Phys. 14, 714 (1946).

<sup>12</sup> G. F. Garlick, *Handbuch der Physik* (Springer-Verlag, Berlin, 1956), Vol. 19, p. 377.

<sup>13</sup> J. Bloem, Philips Research Repts. 13, 167 (1958).

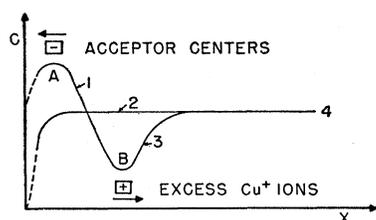


FIG. 24. Acceptor center concentration ( $C$ ) as a function of distance ( $X$ ) from the metal— $\text{Cu}_2\text{O}$  interface. (1) Change in concentration due to application of reverse bias, (2) previous undisturbed level, (3) depletion layer formed as a result of transfer of acceptor center towards the interface, and (4) undisturbed bulk acceptor concentration.

luminescent emission is correlated with electron transitions from the conduction band to the  $B$  level, Fig. 25, within the forbidden band created by copper atom vacancies.

The electroluminescent properties of  $\text{Cu}_2\text{O}$  are not directly analogous to any single material in either of the two general classes of electroluminescent materials (class I semiconducting crystals: Ge, Si,  $\text{SiC}$ , diamond, etc., and class II insulating phosphors:  $\text{ZnS}$ ,  $\text{Zn}_2\text{SiO}_4$ , etc., with various activators Ag, Mn, Cu, etc.).

The emission of light during the existence of a high field in a well-defined barrier region suggests one of the acceleration-collision mechanisms proposed by Piper and Williams<sup>14-16</sup> or by Curie<sup>17</sup> for class II materials. The carrier generation mechanism, however, must be capable of continuous replenishment since light is emitted continuously by dc excitation. This suggests the possibility of carrier injection as proposed by Lehovc *et al.*<sup>18</sup> for class I materials. The existence of an

<sup>14</sup> W. W. Piper and F. E. Williams, *Phys. Rev.* **98**, 1809 (1955).

<sup>15</sup> W. W. Piper and F. E. Williams, *Suppl. Brit. J. Appl. Phys.* **4**, 39 (1954).

<sup>16</sup> W. W. Piper and F. E. Williams, *Phys. Rev.* **87**, 151 (1952).

<sup>17</sup> D. Curie, *J. phys. radium* **14**, 510 (1953).

<sup>18</sup> Lehovc, Accardo, and Jamgochian, *Phys. Rev.* **83**, 603 (1951); *ibid.* **89**, 20 (1953).

injection-acceleration-collision sequence undoubtedly accounts for the lack of comparison with the properties of other common electroluminescent substances.

#### MECHANISM OF ENHANCEMENT OF THE ELECTROLUMINESCENCE BY BIASING

According to the proposed theory of current creep, slow changes in the distribution of  $\text{Cu}^+$  ions and thus in Cu ion vacancies can take place if a strong field exists within the cell. The intensity of the electroluminescence is determined by the presence of Cu ion vacancies (the final stages of the emitting process) in a region of sufficiently high-field strength. It must be

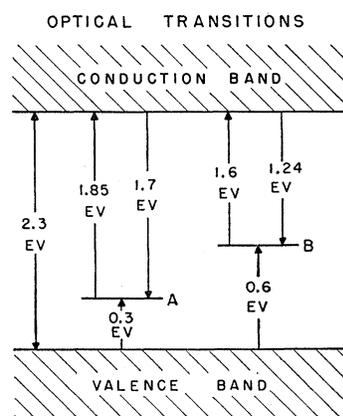


FIG. 25. Luminescent energy band model based upon optical transition data according to J. Bloem.<sup>18</sup>

remembered that the barrier field distribution is determined by the distribution of vacancies within the barrier. Current creep alters the distribution of vacancies, i.e., luminescent centers, in the material and creates a twofold effect on the electroluminescence by (1) changing their availability for excitation, and (2) changing the configuration of the accelerating field in the barrier. The combination of these effects determines the character of the enhancement.

FIG. 22. Cathode ray oscilloscope curves of individual light pulses after reverse biasing. Upper traces are light pulses showing decreasing and increasing pulse trains. Lower trace is ac current with polarity as follows: forward phase upwards, reverse phase downwards.

