Irradiation Effects in Borosilicate Glass

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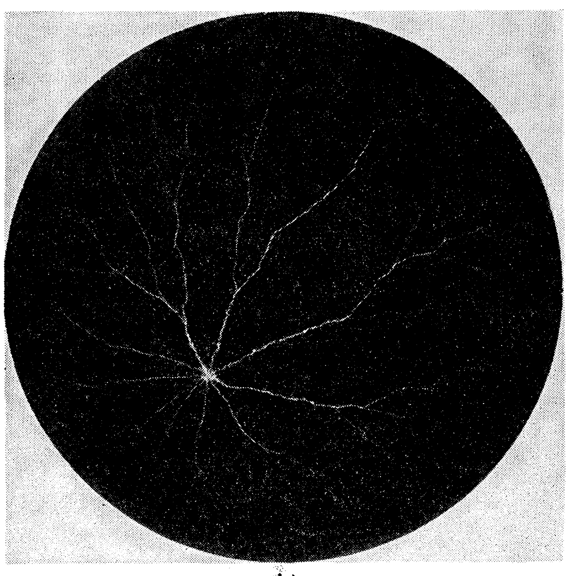
Irradiation of thick samples of borosilicate glass with high-energy electrons introduces space charges into the dielectric, the decay of which is extremely slow at room temperature. The charged dielectric shows a behavior similar to that of an electret; charges are induced on adjacent conductors and short-circuit discharge currents are observed during heating. The nature of the charges of the dielectric, annealing effects, and discharge mechanism were investigated. It is shown that the dielectric contains charges of two types: a negative charge constituted by arrested irradiation electrons and a positive compensation charge.

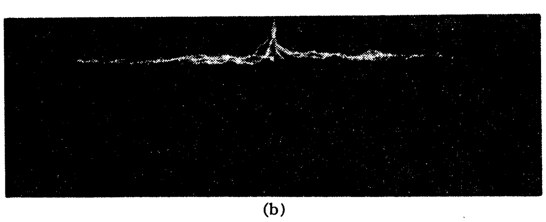
1. INTRODUCTION

IRRADIATION of solid dielectrics with high-energy electrons produces changes of electrical, mechanical, and optical properties. In addition, if the maximum range of the electron beam is smaller than the thickness of the sample, a negative space charge is introduced. The charge may become so high and produce so strong a field that touching of the sample with a pointed piece of metal causes breakdown. This is accompanied by a flash of light. Afterwards a characteristic discharge pattern is found in the dielectric situated in a well-defined plane parallel to its surfaces. The discharge pattern has the form of a Lichtenberg figure with a channel leading to the point where the dielectric was touched by the conductor. With some dielectrics breakdown occurs only during or immediately after irradiation, but with borosilicate glass it can be produced many months after irradiation.[1] Figure 1 shows top and lateral views of a breakdown pattern in borosilicate glass.

These effects are observed with many dielectrics. The behavior of plexiglass has been studied by the author in a separate paper.[2] Direct charge measurements during breakdown and an analysis of the breakdown pattern and process gave strong evidence for the existence of a layer of arrested electrons at a depth corresponding to the plane of the discharge figure. Additional evidence in favor of this point of view is presented in this paper.



(a)



(b)

FIG. 1. (a) Top view of discharge figure in borosilicate sample. (b) Lateral view of discharge figure in borosilicate glass (for this photograph a lateral section of the sample was cut away, to avoid distortion of the picture by the curved lateral surfaces).

2. EXPERIMENTAL

The samples were disks of a commercial borosilicate glass manufactured by Corning Glass Works (glass 7070 of Corning catalog B-83, 1949). Dimensions were: height 1.75 cm, diameter 4.4 cm. Density is 2.1 g/cm^3, dielectric constant 4.

The samples were irradiated with 2-Mev electrons in a Van de Graaff accelerator.[3] Discharge measurements began 1 month or more after irradiation. The total charge intercepted during irradiation was 1.16×10^{-4} coulomb, or 7.6×10^{-6} coulomb/cm^2.

The part of the dielectric penetrated by the electron beam acquires a deep yellow color, owing to the production of color centers. The study of this coloration and its use for dosimetry has been reported by several authors.[4] The coloration extends to a depth of 0.4 cm into the

[1] This effect apparently has not been reported in the literature. However, it has frequently been demonstrated as a lecture experiment by Dr. D. M. Robinson of High Voltage Engineering Corporation, Cambridge, Massachusetts. In this way the author became acquainted with it and later repeated it several times.

[2] B. Gross, J. Polymer Sci. (to be published).

[3] The author expresses his gratitude to Dr. D. M. Robinson, President of High Voltage Engineering Corporation, Cambridge, Massachusetts, who kindly arranged for the irradiation of the samples.

[4] Schulman, Klick, and Rabin, Nucleonics 13, No. 2, 30 (1955); Davison, Goldblith, and Proctor, Nucleonics 14, No. 1, 34 (1956).

dielectric. We consider this value to be the effective range of penetration of the beam. The discharge pattern develops at the end of the colored volume, i.e., again at the depth of 0.4 cm. According to the theory developed in the previous paper,[2] a considerable part of the arrested electrons must be localized at that depth. The Feather formula[5] gives for 2-Mev electrons a maximum penetration of 0.93 g/cm^2 or 0.44 cm for borosilicate glass. The difference between the theoretical and observed values may be due to the fact that the number of electrons penetrating beyond 0.4 cm is too small to produce a visible coloration of the glass.

The specific resistance of the glass is extremely high. Its value at room temperature is very difficult to measure directly. An approximate lower limit for it can be obtained by the following consideration: Since disruptive discharges of charged samples can be produced many months after irradiation, the relaxation time for the decay of the stored irradiation charge by conduction must be at least of the order of one month. With a dielectric constant of 4, this gives for the specific resistance of the sample at room temperature a value of 10^{19} ohm cm. This is higher than previously reported values[6] and nearly reaches the value of 10^{20} ohm cm of amorphous quartz.[7] It is well known that the electrical conductivity of amorphous[8] and crystalline[9] dielectrics is considerably increased during and shortly after photon and particle irradiation. Recently, however, some authors[10] have found in alkali halides a decrease of conductance after irradiation, as compared to the value before irradiation. To see whether such an effect exists in borosilicate glass, a sample of the glass was irradiated with a dose of 2 megarep of gamma rays from a Co-60 source.[11] Irradiation by gamma rays was chosen in preference to electron irradiation because it excluded any possible modification of the results by arrested irradiation particles. However, no difference in resistance between irradiated and unirradiated samples was found between 200°C and 300°C.

The charged dielectric can be expected to show a behavior similar to that of an electret. Therefore the technique developed for the study of electrets[12] was applied. Currents produced in the external circuit and charges induced on adjacent electrodes were measured at room temperature and during heating. For measurements up to 95°C the dismountable capacitor described in earlier publications[12,13] was used. The surface of the sample in contact with the grounded electrode was coated with Aquadag, the other surface was not coated. The capacitor, with sample and heater, was kept in a desiccator with relative humidity below 20%. *No external field was applied.* Therefore all external current and charge effects were produced by space and surface charges in the sample. The system was short-circuited except during the brief instances in which measurements were taken. Current was measured by opening the short circuit and observing the rate of charge of an air capacitor connected in parallel with the sample. Induced charge was measured by opening the short circuit, lifting the measuring electrode, and determining the final charge of the same air capacitor. The readings were taken with an electrometer. For a more detailed discussion we refer to the earlier papers. Figure 2 shows schematically the charges in the dielectric and in the plates, and the direction of the current predominant in most of the measurements. For the sake of simplicity the electrode in contact with the irradiated surface is called electrode *A*; the electrode in contact with the unirradiated surface, electrode *B*. The charge-induction method implies breaking and making of contacts between a metal and a dielectric. Therefore contact electrification can occur. Considerable effects for silica and silica-metal contacts have been reported by Harper.[14] With the present experimental arrangement a systematic effect was also observed. Breaking of the glass-steel contact at 90°C charged the unirradiated glass negatively with approximately 1×10^{-11} coulomb/cm^2. Successive operation of the capacitor led to an accumulation of the charge on the glass. This effect prevented very frequent charge measurements.

For measurements at higher temperatures, the samples were heated in an oven. With this system, only currents could be measured. The distribution of space

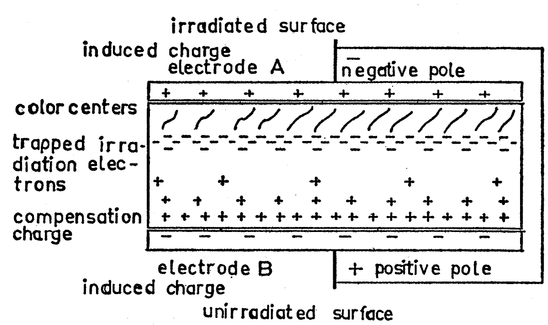


FIG. 2. Charges in sample and electrodes and polarity of currents.

[5] I. Katz and A. S. Penfold, Revs. Modern Phys. **24**, 28 (1952).
[6] J. T. Littleton and G. W. Morey, *The Electrical Properties of Glass* (John Wiley and Sons, Inc., New York, 1933), p. 72.
[7] W. Gnann, Z. Physik **66**, 436 (1930).
[8] J. J. Thomson and McClelland, Proc. Cambridge Phil. Soc. **9**, 15 (1896); D. Nasledow and P. Scharawsky, Ann. Physik **5**, 63 (1929); R. A. Meyer, Office of Naval Research Symposium Report ACR-2, Washington, 1954 (unpublished), p. 93.
[9] W. C. Roentgen, Ann. Physik **64**, 1 (1921).
[10] E. Pearlstein and H. Ingham, Office of Naval Research Symposium Report ACR-2, Washington, 1954 (unpublished), p. 31; K. Kobayashi, Phys. Rev. **102**, 348 (1956).
[11] The samples were irradiated for us at the Naval Research Laboratory, Washington, D. C. The author is greatly indebted to Dr. I. Blifford from the Naval Research Laboratory and Dr. A. Schooley, presently attached to the U. S. Naval Mission to Brazil, who arranged for the irradiation.
[12] B. Gross, J. Chem. Phys. **17**, 866 (1949); Brit. J. Appl. Phys. **1**, 259 (1950).
[13] B. Gross, Report of the Conference on Electrical Insulation, 1948 (unpublished).
[14] W. R. Harper, Proc. Roy. Soc. (London) **A231**, 388 (1955); **A218**, 111 (1953).

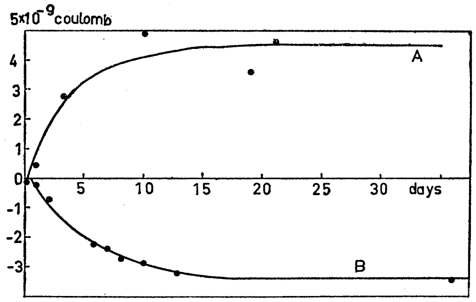


FIG. 3. Charge induction without heating. Curve *A*: charge in electrode *A*. Curve *B*: charge in electrode *B*.

charge inside the dielectric can be determined by a sectioning method associated with current measurements. After irradiation, some of the original samples were cut into two pieces each, the plane of cutting being parallel to the surfaces of the samples. Current measurements were then made with undivided samples and with sections of samples. The cutting operation was easily performed with a small machine using a metal disk as cutting tool and a special abrasive. A method of measurement employing grinding or cutting of dielectric samples has been used by Joffé[15] for the determination of polarization charges in crystals and by other authors for the determination of surface charges of electrets.[16] Creation of new surfaces generally changes existing surface charges and produces new ones, but it does not introduce new space charges or alter the distribution of existing ones. Therefore the sectioning procedure is objectionable for the application of the charge-induction method, but it is appropriate for the study of space-charge distribution by means of discharge current measurements.

3. RESULTS OF MEASUREMENTS

(a) Charge Induction at Room Temperature

Under normal conditions glass is covered by a conducting film of moisture condensed on its surface.[17] The film acts as a shield for the field of the dielectric. Conduction measurements[18] have shown that in an atmosphere of less than 25% humidity most of the film is removed. Therefore induction measurements are possible only in a dry atmosphere. Figure 3 gives as a function of time the charge that developed in the measuring electrode after the capacitor containing a new sample was put into the desiccator. The two curves were made with different samples in reversed positions and corrected for contact electrification. Electrode *A* showed an increasing positive charge and electrode *B* a negative charge. Therefore the irradiated volume contains a predominantly negative charge, and the unirradiated volume contains a positive one (note that the charges of the dielectric are opposite to those of the electrodes). The negative charge must be that of trapped irradiation electrons; then the positive charge is a compensation charge. The presence of the latter is easily understood. During irradiation a strong field builds up between the negative space charge and the support on which the disk rests; eventually it becomes strong enough for the production of prebreakdown phenomena in which positive charge carriers are transferred to the dielectric or negative carriers are extracted from it. The measured charges are lower than the true charge of the dielectric because the field of the two charges of opposite polarity partially cancel each other.

(b) Charge Induction and Discharge Currents above Room Temperature

Heating increases conduction and releases trapped charge carriers; this may be expected to cause the appearance of external discharge currents. Therefore a series of combined induction and current measurements were carried out at increased temperature, up to 95°C, which is the maximum temperature at which the dismountable capacitor could be operated safely. Currents are counted positive if the unirradiated surface becomes the positive pole and the irradiated surface the negative pole. The position of the sample with regard to the measuring electrode is irrelevant for the current measurements. Results of measurements with two samples are shown in Fig. 4.

In the experiment of Fig. 4(a) the irradiated surface of the sample was in contact with the measuring electrode. The temperature was increased rapidly from room temperature (30°C) to 94°C and was kept constant at that value. A discharge current is observed. It reaches a maximum of 3×10^{-12} amp and afterwards decreases. The integral over the current, taken over the entire measuring interval, gives 3.75×10^{-8} coulomb. The charge induced in the measuring electrode (electrode *A*) is positive; it increases from 1×10^{-9} coulomb to 2.3×10^{-8} coulomb.

In the experiment of Fig. 4(b) the unirradiated surface of the sample was in contact with the measuring electrode. The temperature rose more slowly than during the former experiment; after 200 min it reached a constant maximum value of 85°C. In consequence of lower rate of heating and lower final temperature, the discharge current is smaller and reaches its maximum value of approximately 10^{-12} amp much later than before. The current integral is 1.4×10^{-8} coulomb. The charge induced in the measuring electrode (electrode *B*) is negative; it increases from 1.5×10^{-9} coulomb to 1.3×10^{-8} coulomb.

Externally these currents flow from the unirradiated to the irradiated surface (Fig. 2), which becomes the

[15] A. Joffé, *The Physics of Crystals* (McGraw-Hill Book Company, Inc., New York, 1928), p. 114.
[16] Thiessen, Winkel, and Herrmann, Physik. Z. **37**, 511 (1936).
[17] Reference 6, p. 72.
[18] R. F. Field, J. Appl. Phys. **17**, 318 (1946).

negative pole. Therefore, inside the dielectric, negative carriers travel to the irradiated surface and/or positive carriers to the unirradiated surface. Results reported in Sec. 3(c) indicate that both processes occur. The values of the induced charges are much higher than without heating; their polarities are in agreement with the previous findings.

At a dielectric-electrode interface several effects may occur.[19] (a) The charge carriers, piling up at the interface, may be unable to discharge freely. Then the current integral over a given time interval will be equal to the total change of induced surface charge during the same interval. Such a behavior is found at electrode B, within the precision of the current measurements. (b) The carriers may discharge freely. Then, while an external current is observed, the induced charge will not change. This behavior has not been found in our experiments. (c) Only a fraction of the carriers may discharge. Then the change of the induced charge will be smaller than the integral over the external current. This behavior is found at electrode A, where the increase of the induced charge is only 60% of the integral over the current. These measurements give evidence for the existence of positive and negative space charges with different properties.

(c) Complete Discharge at High Temperature

Complete discharge within a reasonable time can be achieved only at temperatures much in excess of those of the previous experiments. So several samples were heated in an oven up to 220°C. Only currents were measured. In these measurements the previously discussed sectioning method was used. Undivided and divided samples were investigated; in the latter case, the sections containing the irradiated volume as well as the sections which lay beyond the range of the 2-Mev electrons were measured. For the understanding of these measurements a short theoretical discussion is necessary.

We consider a very thin layer of arrested charge carriers, of total charge q, situated at distance d_a from electrode A and d_b from electrode B. The charges set up electric fields E_a and E_b, the relation of which is given by $E_a/E_b=-d_b/d_a$. The higher field is directed toward the nearer electrode. Now suppose that these carriers are released in consequence of the increase in temperature. Being able to move, they will travel in the direction of the highest field, i.e., toward the nearest electrode. Concomitantly an external discharge current J is observed. If a charge q moves through a dielectric from one electrode to the other, externally the same charge is recorded; if it moves only over a distance d_a, the externally measured charge is $qd_a/(d_a+d_b)$. Therefore the integral $Q=\int Jdt$ over the discharge current is not equal to, but is smaller than the released charge q, i.e., $Q=qd_a/(d_a+d_b)$. The ratio $(d_a+d_b)/d_a$ is a "conversion" factor. The released charge is obtained from the measured charge by multiplication with this factor. If the distance of the charge layer from electrode A and the value of the released charge remain constant, but the thickness of the sample is changed, the values of current and measured charge change. A more detailed discussion and experimental confirmation of these effects has been given previously.[2] For "thick" layers the situation is more complex; carriers located in the space of the weaker field may reach the farther electrode and cause current reversals.

[19] Such effects have been discussed by B. Gross, J. Chem. Phys. 17, 866 (1949).

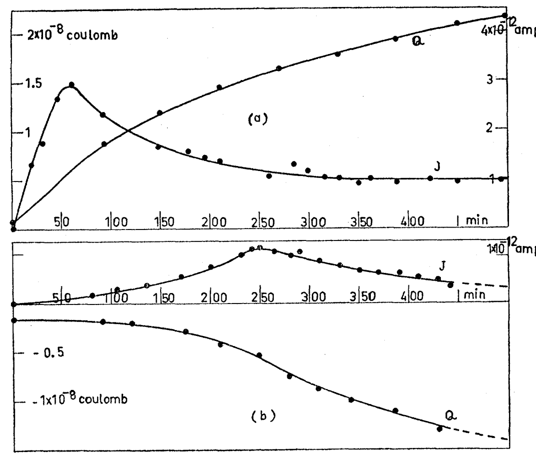


FIG. 4. Current J and induced charge Q during heating. (a) Measuring electrode in contact with irradiated surface of sample. (b) Measuring electrode in contact with unirradiated surface of sample.

Experimental results of current measurements are given in Figs. 5 and 6. Figure 5 refers to samples which contained the entire irradiated volume. Figure 6 refers to samples where the irradiated volume was cut off.

Figure 5, curve I, gives the discharge current for an undivided sample. The current is much higher than before, reaching a maximum of more than 10^{-10} amp; complete discharge is achieved in less than 3 hours. A remarkable feature is the current reversal occurring after 115 minutes. To make sure that the reversal was not a trivial effect caused by a temperature gradient in the sample, the position of the sample was inverted and the experiment repeated, but the reversal persisted. The main current, before the reversal, flows in the same direction as before. We already assumed the existence of a layer of arrested electrons at a distance of approximately 0.4 cm from the irradiated surface. These electrons, when released by the increase in temperature, will travel predominantly toward the nearest electrode, i.e., electrode A, giving the positive current of the experiment. The correctness of this interpretation could be confirmed by a sectioning experiment. The unirradiated part of a sample was cut off a short distance (0.15 cm) below the supposed site of the charge layer; the total thickness after the cut was 0.55 cm. Now

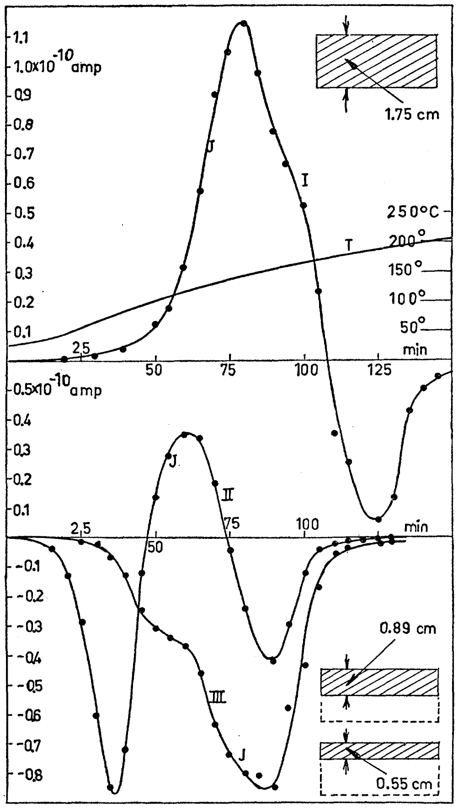


FIG. 5. Current J and temperature T during annealing of samples containing irradiated volume. Curve I—undivided sample. Curve II—section of sample of 0.89 cm thickness. Curve III—section of sample of 0.55 cm thickness. Insets show thickness and position of measured sections; irradiated surface at top.

electrode B is the nearest electrode; the electrons should move predominantly toward electrode B and the current should be reversed. The result of the experiment, shown in curve III of Fig. 5, confirms this expectation. The current has reversed its direction; it is entirely negative and corresponds to the flow of electrons to electrode B. Finally, curve II of Fig. 5 gives results obtained with a sample cut 0.89 cm below the irradiated surface. Now the charge layer is situated approximately halfway between both surfaces. The positive component of current has reappeared, but is still weaker than the negative component. This result indicates that negative space charge extends beyond the depth of 0.4 cm below the surface. Therefore the hypothesis of the very thin layer is not entirely satisfactory.

Figure 6 shows that discharge currents can be drawn from the unirradiated sections too. Therefore these sections, which lie definitely beyond the range of penetration of the electron beam, also contain space charge. The intensities of the currents are smaller than in the experiments of Fig. 5, but the form of the current-time curves is similar to that of Fig 5, curve I. The highest positive and smallest negative currents are obtained from the thinnest sample (thickness 0.3 cm). This sample was also farthest from the irradiated surface (Fig. 6, curve I). The positive current can be explained by transport of positive charge toward electrode B. The source of the carriers must be a high concentration of positive charge so close to electrode B that even with the thinnest samples most of the carriers of the layer migrate toward this electrode. The decrease of positive current with increasing thickness is a geometrical effect caused by a change of the conversion factor. The negative current poses a more difficult problem. It seems to indicate that, in addition to the electrode layer, positive space charge is spread out rather uniformly throughout the volume and contributes carriers migrating toward the top electrode.

Several samples were irradiated with higher radiation doses, up to four times that of the previous experiments. However, except for a slight increase of the reverse current with dose, no significant changes in the current-time curves of undivided samples were observed. Therefore a charge saturation effect exists. This was also found in plexiglass.[2]

4. DISCUSSION

(a) Space-Charge Distribution and Discharge Currents

The experimental evidence pointed to the presence of two types of space charges in the dielectric: (a) a negative charge, consisting of irradiation electrons, for which the maximum concentration is found at a

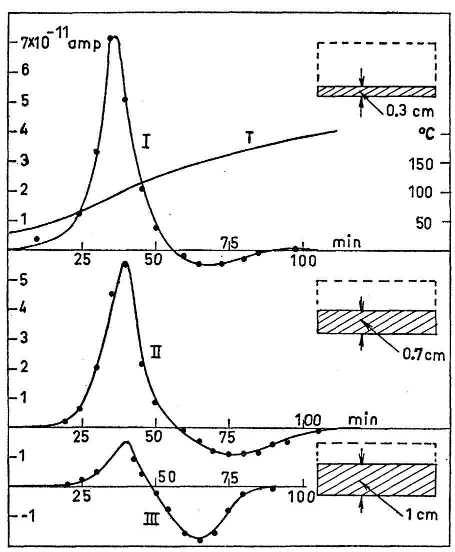


FIG. 6. Current J and temperature T during annealing of samples not containing irradiated volume. Curve I—section of sample of 0.3 cm thickness. Curve II—section of sample of 0.7 cm thickness. Curve III—section of sample of 1 cm thickness. Insets show thickness and position of measured sections; unirradiated surface at bottom.

depth of approximately 0.4 cm below the irradiated surface, but which extends beyond this point toward or even into the unirradiated volume; (b) a positive charge, the compensation charge, which is contained mainly in a space very close to the unirradiated surface. The net charge of the dielectric is small. The charges produce the electric field in the dielectric. The field is obtained by integration over space-charge density. Since the system is shorted, the integral over the field, taken from one electrode to the other, must be zero. Then, with the given charge distribution, the direction of the field in the center section must be contrary to that in the electrode sections. This situation, with field inversion points x_a and x_b, is shown qualitatively in Fig. 7. The appearance of field curves of this type in polarized dielectrics is a classical effect and has been discussed by many authors.[15] Schumann[20] has calculated field curves and discharge current curves under a wide variety of conditions; he specifically considered migration of space-charge layers and electrode effects.

At room temperature, the space-charge distribution behaves as if it was "frozen in." Increase of temperature releases trapped carriers. These begin to move in the field. Negative carriers, originally arrested between the irradiated surface and point x_a, are drawn toward electrode A; positive carriers, between the unirradiated surface and point x_b, are drawn toward electrode B. This transport of charge results in the positive current that predominates in the experiments. However, carriers between x_a and x_b are exposed to the reversed field, which moves negative charge in the direction of electrode B and positive charge in the direction of electrode A. This charge transport corresponds to a reversed, i.e., negative current. The net external current is the sum of the positive and the negative component. It can show one or more reversals, because the two components follow different time functions. The predominance of a negative current at the end of the discharge period indicates that the reversed current component has the longer relaxation time. The fact that charge and field distributions and consequently inversion points may change during the discharge makes a quantitative treatment extremely difficult.

[20] W. O. Schumann, Z. Physik **79**, 532 (1932), Ann. Physik **15**, 843 (1932); Z. Tech. Physik **14**, 23 (1933); Arch. Electrotech. **27**, 155, 241 (1933).

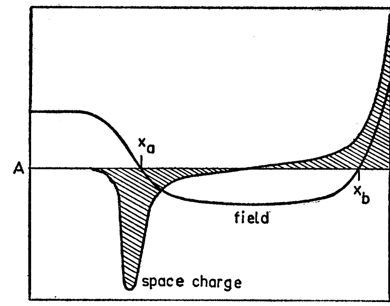


FIG. 7. Qualitative view of space charges and field in the irradiated dielectric.

(b) Released and Intercepted Charge

Electrons from a monoenergetic beam show an absorption in solids which is continuous up to the depth corresponding to the maximum range of such electrons. However, there is some increase in the concentration of arrested electrons toward the end of the range.[5] This is not the distribution inferred from our experiments. The more localized distribution centered at a depth of about 0.4 cm suggested by our experiments may reflect a serious loss of excess negative charge from the irradiated surface of the sample while this surface was exposed to the ionized and conducting air during the irradiation. Charge could be lost from shallow regions by migration to the surface during the irradiation.

Support for this view can be found in a comparison of the discharge-current integral observed with the estimate of the negative charge intercepted by the sample during irradiation. The maximum released charge calculated from the positive and negative charge measurements is 1.2×10^{-6} coulomb. The intercepted charge estimated from the irradiation data is 1.6×10^{-4} coulomb. The 100-fold difference may be the measure of the charge loss during and perhaps shortly after irradiation.

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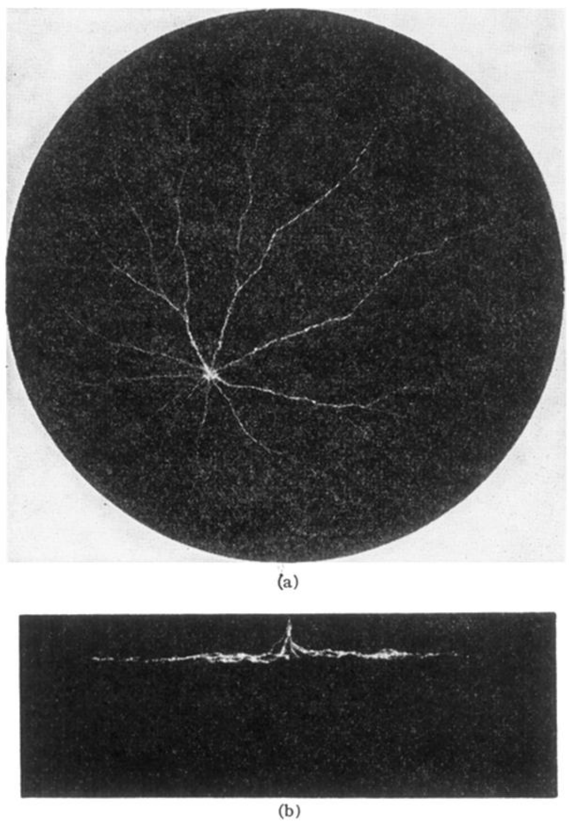

FIG. 1. (a) Top view of discharge figure in borosilicate sample. (b) Lateral view of discharge figure in borosilicate glass (for this photograph a lateral section of the sample was cut away, to avoid distortion of the picture by the curved lateral surfaces).