Polymer Film-Type Channel Electron Multipliers: Their Characteristics and Comparison with Bulk-Type Flexible Multipliers

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Synopsis

Polymer film-type channel electron multipliers (CEMs) were developed and their characteristics investigated in comparison with bulk-type flexible CEM. As film-type CEMs, a paint-coating-type CEM and a solvent-etching-type CEM were fabricated. The paint-coating-type CEM is made by coating a "paint" which is prepared by dissolving in a solvent an electronically conductive polymeric composition having a high secondary electron emission yield. Up to the present study the mean gain of the film-type CEM, in spite of the lower resistivity of the dynode, seems to be slightly more dependent on the count rate than that of the bulk-type CEM made of the same material. However, the convenience of fabricating the dynode film by coating the dynode-forming paint on the internal surface of any shaped tube or a flexible polymer tube would overcome the slight disadvantage mentioned above.

INTRODUCTION

A channel electron multiplier (CEM) comprises a continuous dynode which emits secondary electrons and has proper resistivity as shown in Figure 1, in contrast with a conventional discrete dynode-type multiplier, and has excellent characteristics of simple structure, small size, light weight, low power consumption, high gain, and low background noise.[2] The CEM is widely utilized as a highly sensitive detector for charged particles (electrons and ions) and high-energy photons (vacuum UV and x-ray) and has been used in the fields of electron spectroscopy, surface science, and space science, etc., in recent years. In general, there are two types of CEMs; one is a thin film-type CEM consisting of a hollow tube only the internal wall of which has proper resistivity, and the other is a bulk-type CEM consisting of a hollow tube the whole of which has proper resistivity. Ordinarily the thin film type is made of high-lead glass and the bulk type is made of ceramics such as $PbTiO_3$ or $ZnTiO_3$.[2,3]

In studying the secondary electron emission (SEE) from polymers, we have developed a highly sensitive "flexible CEM" which is durable against mechanical shock and has excellent molding qualities. This flexible CEM is a bulk-type CEM made of flexible thermoplastics as shown in Figure 3(a) which has already been reported in detail together with the SEE characteristics of various polymers.[1] This flexible CEM has been installed on sounding rockets and artificial satellites, and has been used as a detector for electrons and photons in space.[4]

In this paper, polymer film-type CEMs made by utilizing the solubility in a

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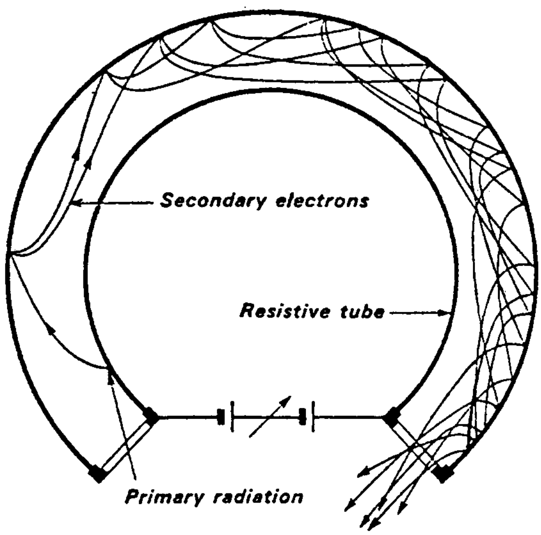
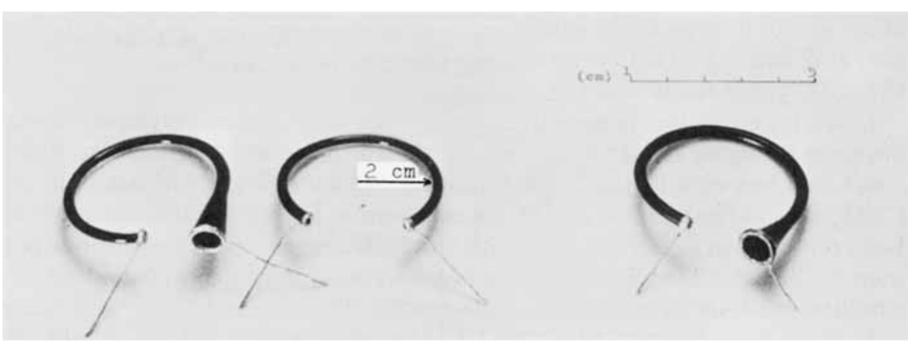


Fig. 1. Principle of curved channel electron multiplier.[2]

solvent and the film-forming ability of polymeric materials are described. This polymer film-type, classified as thin film-type CEM, is of two kinds: (a) a paint coating-type CEM (PC-CEM) and (b) a solvent etching-type CEM (SE-CEM), as shown in Figure 2. The PC-CEM has a continuous dynode of polymer film coated on an internal wall of a hollow electrical insulating tube, as shown in Figure 3(b); this film is made by coating and drying a "paint" consisting of an electronically conductive polymeric composition dissolved in a solvent. In this PC-CEM a free insulating material such as glass, ceramics, or high polymer, etc., can be used as the tube material. On the other hand, the SE-CEM, as shown in Figure 3(c), has a polymer dynode made by lowering the electrical resistivity of an internal wall of the tube by the solvent-etching process. The solvent is poured into the tube for a predetermined time, and the tube material is made



(a) (b)

Fig. 2. Polymer film-type channel electron multipliers: (a) paint coating-type CEM; (b) solvent etching-type CEM.

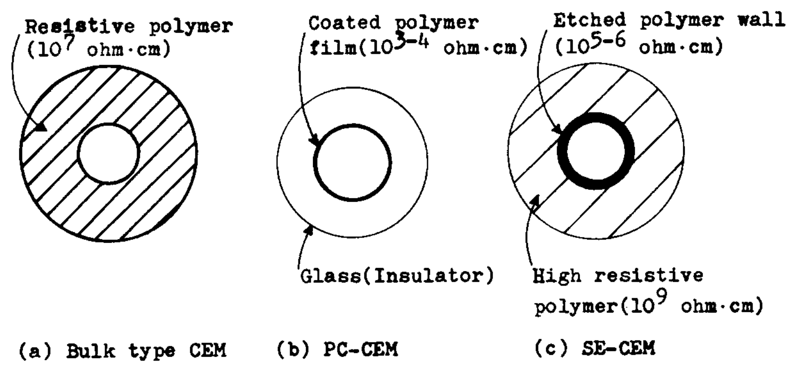


Fig. 3. Cross-sectional models of polymeric channel electron multiplier tubes.

of an electronically conductive polymeric composition having high resistivity and SEE capability. This tube is flexible; its dynode never peels off and is stable because it is of the same material as the tube.

In CEMs made of inorganic materials, both thin film type and bulk type, could hitherto not be made of the same materials. In the polymeric CEMs whose materials have excellent molding qualities and film-forming abilities, both CEMs have for the first time been able to be made of the same materials. The polymer film-type CEMs are made of the same material as the bulk-type flexible CEM already reported in reference 1; the characteristics of these film-type CEMs are not only described in this paper, but are also compared for the first time with that of the bulk type made of the same materials.

EXPERIMENTAL

A dynode material is an electronically conductive polymeric composition consisting of a matrix polymer and conductive particles.. A plasticized compound consisting of poly(vinyl chloride) (PVC) and polyurethane (PU) having high SEE yield δ is selected as the matrix polymer, and sodium 7,7,8,8-tetracyanoquinodimethanide (NaTCNQ) and carbon black (CB) are used as the conductive particles. The NaTCNQ is an organic semiconductor of volume resistivity of 10^5 Ω·cm which is thermally stable and molecularly partially dispersible in the matrix polymer, and the CB are conductive particles of resistivity 0.2 Ω·cm. Carbon black is widely used for polymers and is dispersed granularly in the polymers. PVC, PU, NaTCNQ, CB, and stabilizer are mixed and kneaded by heated rollers and then formed into a sheet 1.5 mm thick as an electronically conductive polymeric composition.

Fabrication Method for Paint Coating-Type CEM (PC-CEM)

The electronically conductive polymeric composition prepared is dissolved and dispersed in ten times its volume tetrahydrofuran (THF), and this forms the "paint." The paint is poured into a circular glass tube having an internal diameter of 3.2 mm, length of 10 cm, and curvature radius of 20 mm, is coated on its internal surface, and then dried at 100°C in a vacuum oven. Both glass tubes having a funnel or no funnel are used, as shown in Figure 2(a). The funnel is 1.5 cm in length and has an entrance aperture of 6.5 mm in internal diameter.

As the electrode, colloidal graphite (Aquadag) is first coated to both ends of the PC-CEM tube to obtain ohmic contacts, and silver wire wound on the coated graphite film is fixed by a silver paint with epoxy resin binder.

Fabrication Method for Solvent Etching-Type CEM (SE-CEM)

The above-mentioned sheet of electronically conductive polymeric composition having a resistivity of 10^9 Ω·cm is cut into small pellets, and then these are shaped into a hollow tube through a die by the extrusion molding method. The tube obtained by this process has an internal diameter of 1.2 mm, an external diameter of 3.6 mm, and a length of 11 cm including a funnel. The funnel is 1 cm in length and has an entrance aperture of 8 mm in internal diameter. For the solvent etching process the THF solvent is poured into this tube for about 5–30 sec, the tube is dried by hot air and then is sufficiently dried at 100°C in a vacuum oven. As the result of this etching process, the resistivity of the internal wall of the tube is lowered in range of the depth of 100–150 μm. The electrode of this SE-CEM tube is attached by the same method as the PC-CEM mentioned above. The tube is bent in a circular arc with a radius of 20 mm to prevent the ionic feedback effect. A photograph of an example of SE-CEM is shown in Figure 2(b).

Measuring Method for Multiplication Characteristics

The polymer film-type CEMs are mounted in a circular arc 20 mm in radius in order to avoid the ionic feedback effect. An accelerating voltage of 3 kV is applied to the electrodes of the CEM, and its gain characteristics are measured in the pulse-counting mode under vacuum ($<10^{-5}$ Torr) by using the demountable apparatus and method shown in the previous paper.[1]

RESULTS AND DISCUSSION

Electrical Resistance

The electrical resistance of the PC-CEM is about 10^8 to 10^9 Ω, and the volume resistivity ρ of this coated dynode film is estimated to be about 10^3 to 10^4 Ω·cm from its thickness of 10 to 20 μm. The volume resistivity of the internal wall of the tube is more uniform than that of the bulk type. Though the coated dynode film of this PC-CEM is made by coating a "paint" consisting of the electronically conductive polymeric composition of 10^7 Ω·cm and THF, the value of volume resistivity of its dynode film is 10^3 to 10^4 Ω·cm and is three to four orders of magnitude smaller than 10^7 Ω·cm.

Otherwise, the SE-CEM also has a resistance of about 10^8 to 10^9 Ω, and the volume resistivity of this etched dynode film is estimated to be about 10^5 to 10^6 Ω·cm from its thickness of 100 to 150 μm. A decrease in the resistivity of the tube wall by solvent etching is observed for the paint containing only CB and also for the paint containing both CB and NaTCNQ. However, decrease in resistivity has not been observed for the paint containing only NaTCNQ. During the process of solvent etching, the internal surface of the tube is slightly dissolved out into the THF solvent, swells by absorbing the solvent, and reduces its viscosity. Carbon black particles included in the compositions tend to cohere with each other, and the resistivity seems to be reduced by the formation of conductive channels. Thus, the resistance of the SE-CEM dynode is lowered from 10^{11} ohm ($\rho = 10^9$ Ω·cm) to 10^8 to 10^9 Ω by this solvent-etching process. As the volume resistivity of this dynode wall is estimated to be 10^5 to 10^6 Ω·cm as shown above, the value of the volume resistivity is three to four orders of magnitude smaller than the resistivity of 10^9 Ω·cm before the solvent etching. The resistivity of this SE-CEM is also uniform in each part of the dynode as well as the PC-CEM. Both dynode films of PC-CEM and SE-CEM are surmised to have a similar orientation and dispersion state of conductive particles in the compositions. According to a scanning electron microphotograph (×3000), the dynode surfaces of both the PC-CEM and the SE-CEM show a surface state having similar roughness different from that of the bulk type.

The voltage–current characteristics of both the PC-CEM and the SE-CEM are ohmic in a wide range, and the electric field strength is 250 to 300 V/cm at the operating voltage of 3 kV.

The temperature dependence of the resistance of these CEMs is very small, as shown in Figure 4. The temperature coefficient of the CEM having a resistance of about 10^9 Ω is slightly negative, and that of about 10^8 Ω is slightly positive. This temperature stability of resistance is very excellent in comparison with the bulk-type CEM having a thermistor B constant of 3000 K.

Gain Characteristics

Polymer Film-Type CEMs

The count rate dependences of the mean gain $\overline{G}$ and the output current ratio I_0/I_d are shown in Figures 5 and 6 for the PC-CEM and the SE-CEM, respectively, where I_0 is the output current and I_d is the dc current of the tube at the time of no count. The mean gain of the PC-CEM is (3–5) × 10^7 at the applied voltage of 3.0 kV, and that of the SE-CEM is (0.7–1) × 10^8. It would be due to the larger internal diameter of the tube than that of the SE-CEM that the mean gain of the PC-CEM is slightly low. The count rate dependence of the mean gain is excellent in both PC-CEM and SE-CEM, and the lowering of mean gain is very little in spite of the increase in the count rate N_c in the range of less than 10^4 counts/sec.

On the other hand, the maximum output current ratio $(I_0/I_d)_{max}$ of the SE-CEM having a resistance of about 10^9 Ω reaches 10^{-1}, which would be the upper limits expected theoretically, but the output current ratio of both CEMs having a resistance of about 10^8 Ω has a tendency to saturate at the smaller value of one order of magnitude than the SE-CEM of 10^9 Ω, and the maximum value $(I_0/I_d)_{max}$ is about 10^{-2}. This is due to the fact that despite of the lower resistance (about 10^8 Ω) and gain, the value of I_0/I_d tends to saturate at nearly the same count rate of about 10^4 counts/sec, as is the case of the SE-CEM having a resistance of 10^9 Ω. This phenomenon is based on the microscopic nonuniform structure of the resistive dynode film of the CEM; this shows that the resistivities of microdomains in both dynode walls of the PC-CEM and the SE-CEM are very

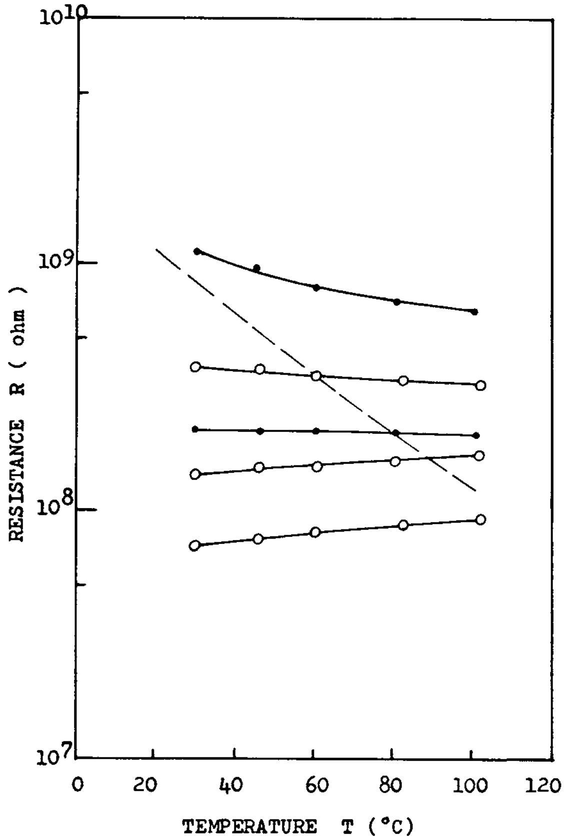


Fig. 4. Temperature dependence of electrical resistance of polymer film-type CEMs. (○) PC-CEM; (●) SE-CEM; (- - -) bulk type.

similar, regardless of the macroscopic resistivities based on the formation of conductive channels in the compositions. These characteristics based on the resistivities and structures of dynode films of both CEMs will be revealed in detail by further study.

Gain Characteristics of Carbon-Type PC-CEMs

In the previous paper[1] it has already been reported that the count rate dependence of output current ratio of the bulk-type CEM (NaTCNQ + carbon-type FCEM) in which the conductive particles are both NaTCNQ and CB is more excellent than that of the CEM (carbon-type FCEM) in which the conductive particles are only CB, and that the maximum output current ratio also is more than 10^{-1}. The carbon-type FCEM has high gain of 10^8 but a very low $(I_0/I_d)_{max}$ of 10^{-5} to 10^{-3}, ordinarily. One of the most excellent characteristics of these carbon-type FCEMs was described in the previous paper and has shown a value of $(I_0/I_d)_{max}$ of 3×10^{-3}.

The count rate dependence of the output current ratio of the carbon-type PC-CEM is shown in Figure 7, here PVC + PU or PU has been used as the matrix polymer. These $\overline{G}$–N_c characteristics show a similar tendency to that of the bulk type but are characterized by gently dropping slopes of the gain with increase

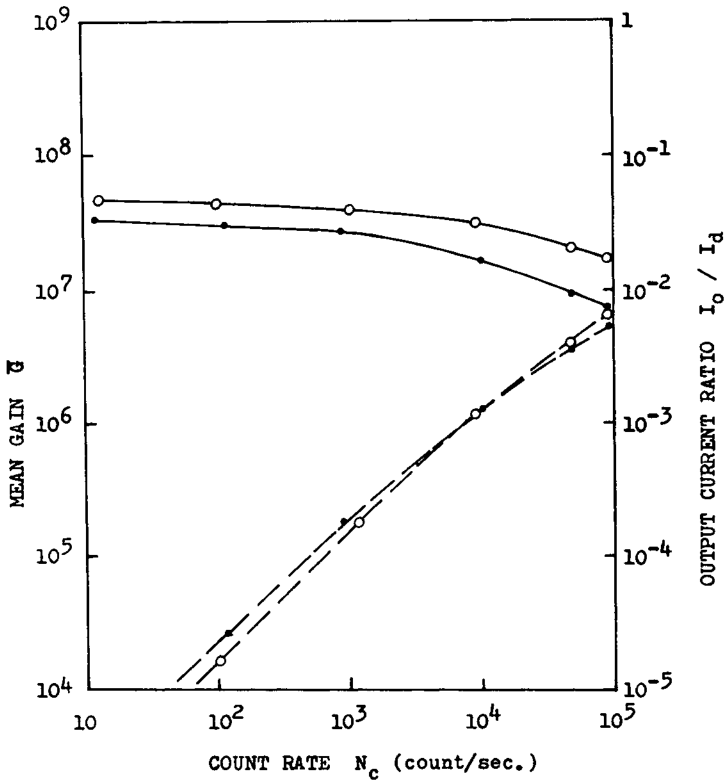


Fig. 5. Count rate dependence of mean gain and output current ratio of paint coating-type CEMs: $V_a = 3.0$ kV; (—) $\overline{G}$; (- - -) I_0/I_d; (○) $R = 7.35 \times 10^7\ \Omega$; (●) $R = 1.44 \times 10^8\ \Omega$.

in the count rate compared with the bulk type. This is probably due to the relaxation effect of the charge-up of microdomains in the internal wall of the tube by the SEE, and the relaxation effect is considered to result from the very low resistivity ($\rho = 10^3$ to $10^4\ \Omega$·cm) of this PC-CEM dynode in comparison with that ($\rho = 10^7\ \Omega$·cm) of the bulk-type CEM. A carbon-type PC-CEM having excellent count rate dependence of gain may be made in the future by improving the kind, the contents, and the dispersion states of CB in the polymeric composition.

Comparison of Film Type with Bulk Type

The bulk-type CEM is made of a polymeric composition which consists of PVC, PU, NaTCNQ, CB, and stabilizer, has a volume resistivity of $10^7\ \Omega$·cm, and is formed into the tube shape having a funnel by the extrusion molding method similar to the SE-CEM tube. Both PC-CEM and SE-CEM are made of the same materials as the bulk type. The sizes and characteristics of these CEMs are tabulated in Table I.

The temperature coefficient of resistance is smaller for the film type than for the bulk type, and the resistance of the film type is thermally more stable. The mean gain of the bulk-type CEM is 1×10^8 at the applied voltage of 3.0 kV. In comparison, the mean gain of the PC-CEM is lower, and that of the SE-CEM is nearly equal. The maximum output current $(I_0)_{max}$ of the bulk type is about

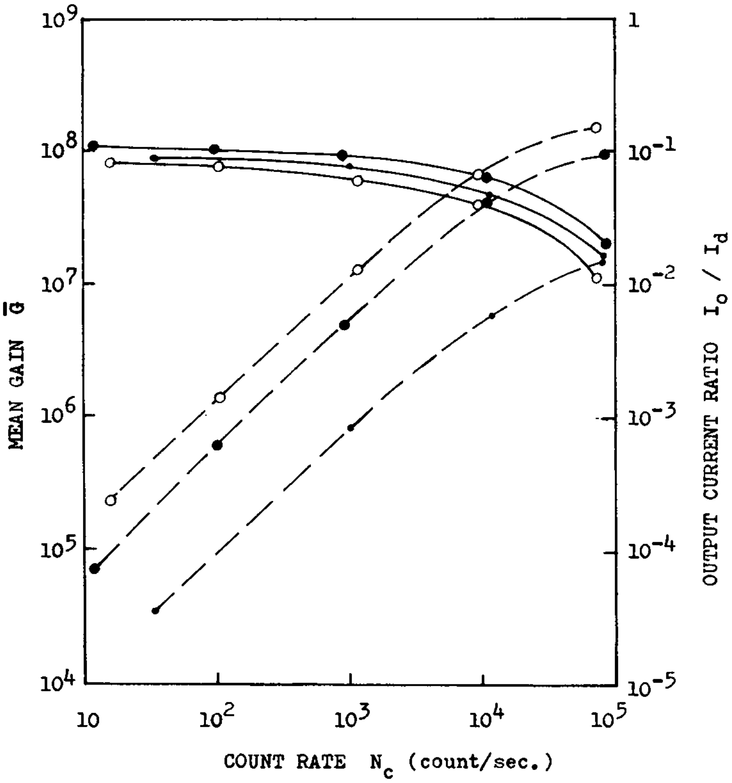


Fig. 6. Count rate dependence of mean gain and output current ratio of solvent etching-type CEMs: V_a = 3.0 kV; (—) $\overline{G}$; (- - -) I_0/I_d; (·) R = 2.1 × 10^8 Ω; (●) R = 1.1 × 10^9 Ω; (○) R = 3.4 × 10^9 Ω.

TABLE I
Characteristics of Polymeric CEMs Made of PVC, PU, NaTCNQ, and CB

	Bulk-type flexible CEM	Polymer film-type CEM	
		PC-CEM	SE-CEM
Internal diameter, mm	1.2	1.4	1.2
External diameter, mm	3.6	3.0	3.6
Tube length, cm	11	11.5	11
Mean gain (V_a = 3 kV)	1 × 10^8	(3–5) × 10^7	(0.7–1) × 10^8
Maximum output current, A	10^{-6}	(2–4) × 10^{-7}	(2–4) × 10^{-7}
Background noise, counts/sec	<0.1	<0.1	
Resistance, Ω	about 10^9	about 10^8–10^9	
Temperature coefficient of resistance (B constant), K	3000	<1200	

10^{-6} A and is much better than that of the film type, (2–4) × 10^{-7} A. As the value of $(I_0)_{\max}$ is given by $(e{\cdot}\overline{G}{\cdot}N_c)_{\max}$, it depends on the $\overline{G}$–N_c characteristics. The $\overline{G}$–N_c characteristics are closely related to the mechanism of the SEE and the electronic conduction in the dynode wall of CEM. In the dynode wall of these polymeric CEMs, the mechanism of the SEE and the electronic conduction is represented by the schematic model as shown in Figure 8. In the figure, secondary electrons are mostly emitted from the matrix polymer (PVC + PU) having high SEE yield,[1] and positive holes generated by its SEE are neutralized by

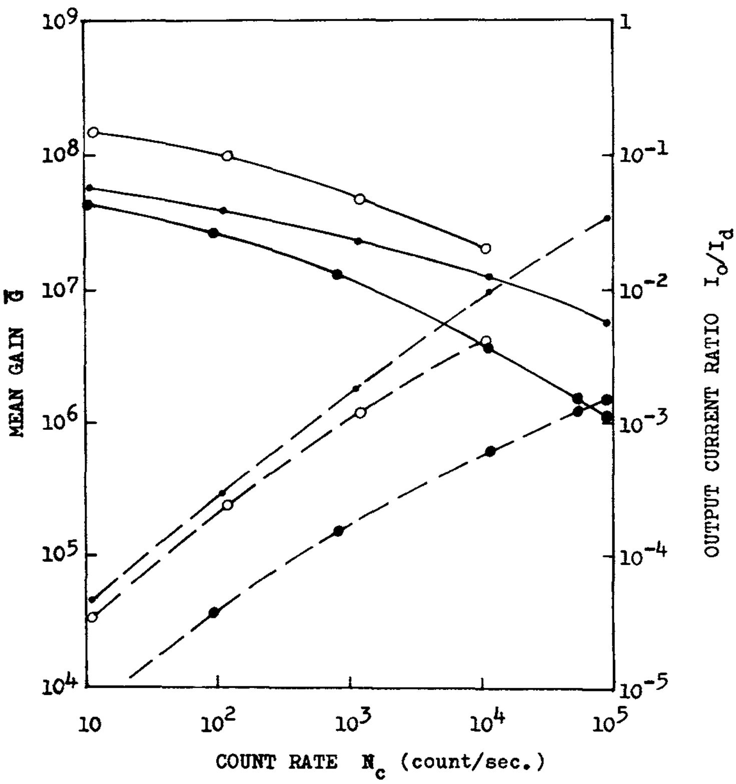


Fig. 7. Count rate dependence of mean gain and output current ratio of carbon-type PC-CEMs: $V_a = 3.0$ kV; (—) $\bar{G}$; (- - -) I_0/I_d; (•) $R = 1.3 \times 10^8\ \Omega$ (PU), no funnel; (○) $R = 3.8 \times 10^8\ \Omega$ (PVC + PU), no funnel; (●) $R = 2.7 \times 10^8\ \Omega$ (PVC + PU), with funnel.

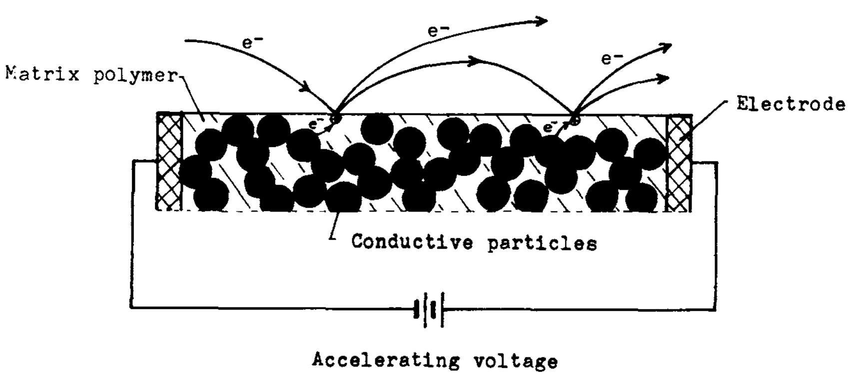


Fig. 8. A schematic model for the mechanisms of secondary electron emission and electronic conduction in the dynode wall of the polymeric CEM.

electrons injected from conductive channels consisting of conductive particles in the polymeric composition. Therefore, the material having high conductivity or high electron mobility would have an excellent count rate dependence of the gain because of its high rate of electron injection. However, the above results do not agree with the inference that the (I_0/I_d)–N_c characteristics of the film type having low resistivity would be more excellent than that of the bulk type having high resistivity because of the low charge-up effect in its dynode wall. This shows that the resistivity of microdomains in the polymeric dynode wall is not low in spite of the very low resistivity of the film-type dynode compared with the bulk type. This means that the enormous difference between the dynode resistivities of the film type and the bulk type is not due to the difference between the two resistivities of microdomains in the polymeric compositions, but is based on the degree of forming conductive channels by the connection state of CB particles in the polymeric composition, including conductive particles of the same content. This difference is also supported by the above-mentioned temperature dependence of resistance and the scanning electron microphotograph of the dynode surface. Therefore, if the film-type CEM is made of an intrinsic semiconducting polymer having high SEE yield, it would have an excellent count rate dependence of the gain.

The background noises of these polymeric CEMs are very low, as shown in Table I. For more comparison of the characteristics and theories of the film-type CEM with that of the bulk-type CEM, further detailed investigations would be required.

The experimental results for the polymer film-type CEM have been described and discussed in comparison with the bulk-type CEM. Considering the residual gas pressure under vacuum, the polymer film-type CEM is desirable for a detector used in vacuum-sealed structures because the quantities of polymeric material used in the CEM is very small. The CEM described in this paper is one example of the polymer film-type CEM, and the development of further excellent polymeric dynode material having thermal stability, low out-gas, and long life, etc., would be desired in the future. The convenience of obtaining the dynode film by coating the dynode paint on the internal surface of any preshaped tube or a flexible polymer tube would facilitate wide utilization of the dynode-forming paint, and the polymer film-type CEM would be manufactured very easily and economically. Besides, these materials could also be utilized as dynode materials for a channel plate whose channels are arrayed, and this channel plate may be used, for example, as an image intensifier.

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