JOURNAL OF APPLIED POLYMER SCIENCE VOL. 21, 2721-2733 (1977)

Secondary Electron Emission from Polymers and its Application to the Flexible Channel Electron Multiplier

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Synopsis

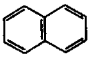
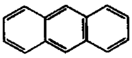
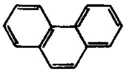
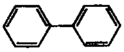
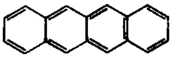
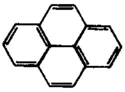
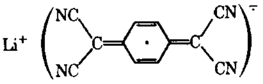
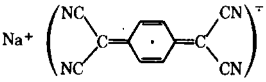
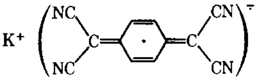
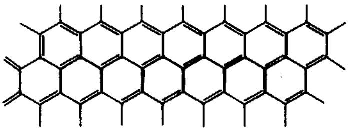
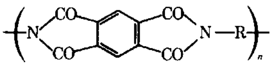
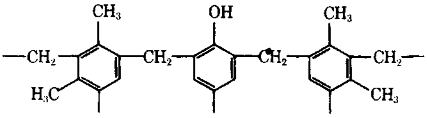
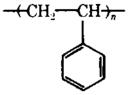
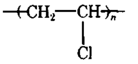
The basic characteristics of secondary electron emission (SEE) from various organic compounds have been investigated, and a channel electron multiplier with high gain and flexibility has been developed. The maximum SEE yield is higher for the aliphatic compound than for the aromatic, and is higher for the organic solid with high ionization potential. By studying the SEE yields from the electron-conductive polymeric compositions which consist of plasticized poly(vinyl chloride) and electroconductive particles (NaTCNQ or carbon black), it is shown that the SEE yield depends mainly on the characteristics of the matrix polymer and is almost independent of the addition of electroconductive particles which inherently have low SEE yields. Adding less than 5% stabilizers to these polymeric compositions has little effect on the SEE yields. A flexible channel electron multiplier (FCEM) made of the electron-conductive polymeric composition shows the following characteristics: gain $\simeq 10^8$ (applied voltage of 3 kV); rise time $\simeq$ a few nanoseconds; background count rate < 0.1 cps; and maximum output current $\simeq 10^{-6}$ A. As a photon detector in the vacuum UV region, the FCEM shows a threshold value of 8.4 eV for photoelectric emission.

INTRODUCTION

The study of secondary electron emission (SEE) from organic compounds was first carried out by Matskevich et al.,[1] and the general characteristics were reported by Martsinovskaya.[2] A detailed report on SEE from some aromatic hydrocarbons by Bubnov et al.[3] showed that the SEE yield from anthracene depends on both the crystal state and the angle of incident primary electrons. Willis et al.[4] studied the relation between the normalized SEE characteristics of some polymers and their densities. Detailed studies and theories on SEE from organic compounds have not yet been reported. The authors have tried to review and analyze the trend of the maximum SEE yields from various organic compounds on the basis of these reported data. This paper describes the SEE characteristics not only for pure polymers, but also for electron-conductive polymeric compositions comprising polymer, conductive particles, and stabilizer.

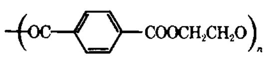
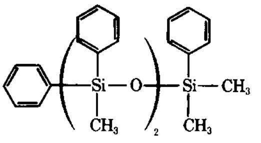
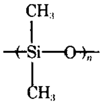
As an application of the SEE effect of electron-conductive polymeric com-

TABLE I
Maximum SEE Yields of Various Organic Compounds
I. Molecular Crystal

Abbre-viation	Material	Chemical structure	δ_{max}	$E_{p\,max}$, eV	Ref[a]
BE	Benzene		1.66	200	2
NA	Naphthalene		1.52	300	2
AN	Anthracene		1.38	400 200	2 3
PH	Phenanthrene		1.55	300	2
DI	Diphenyl		1.7	400	2
TE	Tetracene		1.46	200	3
PY	Pyrene		1.50	250	3
LT	LiTCNQ		1.33	200	EX
NT	NaTCNQ		1.6	200	EX
KT	KTCNQ		1.6	200	EX
C	Graphite		1.0	300	1
IC	Ice	H—O—H	2.3	300	2
		II. Polymers			
PI	Polyimide		2.1 1.5	150 180	4 EX
XY	Xylene resin		1.8	200	EX
PS	Polystyrene		3.0 2.1	250 250	4 1
PE	Polyethylene	$-(CH_2-CH_2)_n-$	2.85	250	1
PVC	Poly(vinyl chloride)	 $-(CH_2-\underset{Cl}{CH})_n-$	2.2	250	EX

continued

TABLE I

Abbreviation	Material	Chemical structure	δ_{max}	E_p max, eV	Ref[a]
PTFE	Poly(tetrafluoroethylene)	$-\!(CF_2-CF_2)_n\!-$	3.0	300	4
PET	Poly(ethylene terephthalate)		4.8 3.2	175 250	4
TSi	Tetraphenyltetramethyltrisiloxane		2.0	200	7
PDSi	Poly(dimethylsiloxane)	 $-\!(\overset{CH_3}{\underset{CH_3}{Si}}-O)_n\!-$	2.35	200	EX

[a] EX = Experimental data by authors.

positions, a flexible channel electron multiplier (FCEM) has been fabricated.[5,6]

In general, there are two types of channel electron multipliers (CEM); one is a thin film-type CEM made of lead glass and the other, a bulk-type CEM made of ceramics such as $BaTiO_3$ and $ZnTiO_3$. This FCEM is a bulk-type CEM made of polymeric composition and can be easily fabricated by an extrusion-molding method because of the excellent molding qualities of the electron-conductive polymeric composition. As compared with the fragile CEM made of glass or ceramics, the FCEM resists mechanical shock and vibration and can be set in any curvature in order to avoid "ionic feedback." In this paper, the performance and advantages of FCEM are also described.

SECONDARY ELECTRON EMISSION YIELD

Experimental

The SEE yields from polymers were measured not only for pure polymers, but also for electron-conductive polymeric compositions applicable to the materials for FCEM. The SEE yields from organic semiconductors which could be used as conductive particles in the polymer matrix were also measured.

In preparing the test samples, crystal powders of organic semiconductors (LT, NT, and KT shown in Table I) were molded into tablets 1.5 mm thick and 1 cm in diameter under high pressure, and polymers with high resistivity (PI, XY, PVC, and PDSi shown in Table I) were made into films a few microns thick on aluminum plates.

As raw materials for test samples of electron-conductive polymeric compositions applicable to FCEM, the following compounds were selected. As matrix polymer, poly(vinyl chloride) (PVC) was selected because of its high SEE capability and excellent blending and molding qualities. As polymeric plasticizer, polyurethane (PU) was employed because of its low vapor pressure and effectiveness on flexibility. As stable electroconductive particles for importing

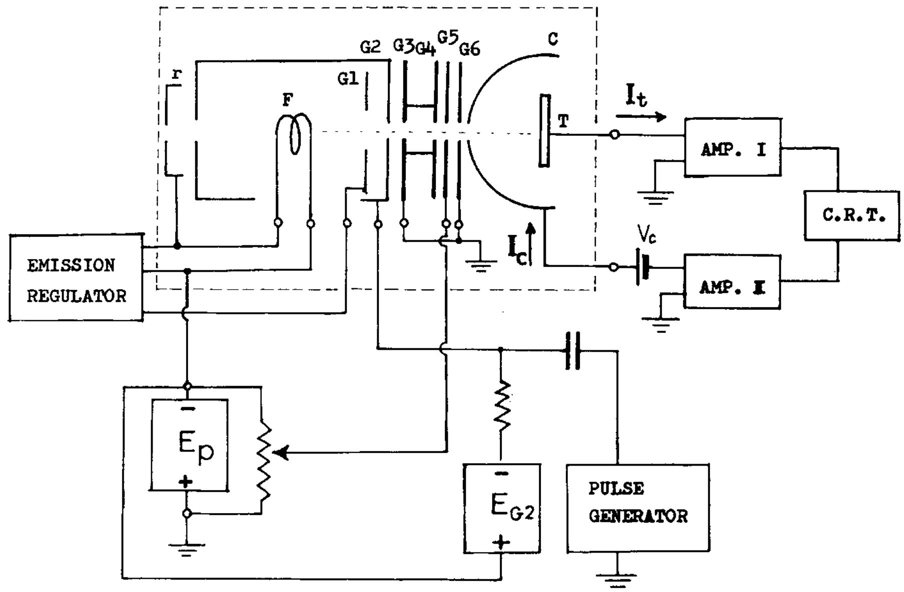


Fig. 1. Apparatus for measuring secondary electron emission yield.

electronic conductivity to the polymer, sodium 7,7,8,8-tetracyanoquinodimethane (NaTCNQ) or carbon black was used. The former is an organic semiconductor which has a volume resistivity of 10^5 ohm·cm and molecular dispersibility in the polymer matrix; and the latter has a resistivity of 0.2 ohm·cm and granular dispersibility. PVC, PU, electroconductive particles (NaTCNQ or carbon black), and stabilizers (tribasic lead sulfate and barium cadmium coprecipitation salts of lauryl acid) are blended by heated rollers and then formed into a sheet 1.5 mm thick. Each sample is cut into a disk 1 cm in diameter and is mounted on a target.

The SEE yield is measured by the dc method for the organic semiconductors, and by the pulse beam method for the polymers and their compositions in order to avoid charge buildup on the sample surface. The block diagram of the pulse beam method is shown in Figure 1. The electron beam from the cathode F is accelerated to E_p eV by an electron lens system (G_1–G_6) and bombards the target T. The electron beam current used was less than 10^{-9} A, and its pulse width was 1 msec. The secondary electrons emitted from the sample are collected at the collector C and are measured; measurement was carried out under pressure less than 10^{-8} torr.

The SEE yield δ is defined by the following equation:

$$\delta = I_c/(I_c - I_t) \qquad (1)$$

where I_c and I_t are the collector current and the target current, respectively.

Results and Discussion

The maximum SEE yields $\delta_{\max}$ and the corresponding primary electron energy $E_{p_{\max}}$ of some organic compounds are shown in Table I. Most of the $E_{p_{\max}}$ values

TABLE II
Maximum SEE Yields and Ionization Potentials of Various Organic Solids

Material	δ_{max}	I_s, eV	Ref.	π_e	σ_b	σ_b/π_e
Benzene	1.66	—	—	6	6	1.0
Naphthalene	1.52	6.76 6.84	11	10	8	0.8
Anthracene	1.38	5.65	11	14	10	0.71
Phenanthrene	1.55	6.45	11	14	10	0.71
Tetracene	1.46	5.28	11	18	12	0.67
Pyrene	1.50	5.6 5.8	11	16	10	0.62
Diphenyl	1.7	—	—	12	11	0.92
Graphite	1.0	4.83	12	∞	0	0
Polyethylene	2.85	8.5	9	0	6	∞
Poly(vinyl chloride)	2.2	6.0	10	—	—	—
Polystyrene	2.1	7.0	10	6	11	1.83
NaTCNQ	1.6	5.6	8	—	—	—

are 200–300 eV, and the δ_{max} values are higher for aliphatic than for aromatic compounds.

In simple hydrocarbon compounds, the relationship between the maximum SEE yields and the chemical bonds is shown in Table II and is graphically plotted in Figure 2. In this Figure, π_e is the number of π electrons in the molecule and σ_b is the number of σ bonds existing in the outside of the π electron clouds. It is evident that the higher the value of σ_b/π_e, the higher the maximum SEE yield. This is exemplified by comparison between diamond and graphite both of which consist of the same carbon atoms. The former is a σ bond crystal with δ_{max} of 2.8, and the latter is a π bond crystal with δ_{max} of 1.0. As seen from the difference of conductivity between diamond and graphite, the electronic conduction of the organic compound can be attributed to the π electrons in the molecule, and it

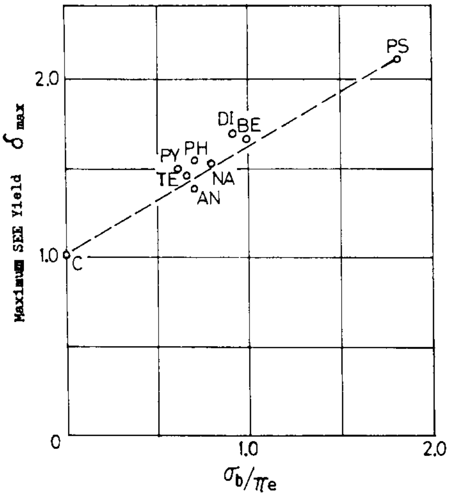


Fig. 2. Relationship between maximum SEE yield and chemical bonds in simple hydrocarbons.

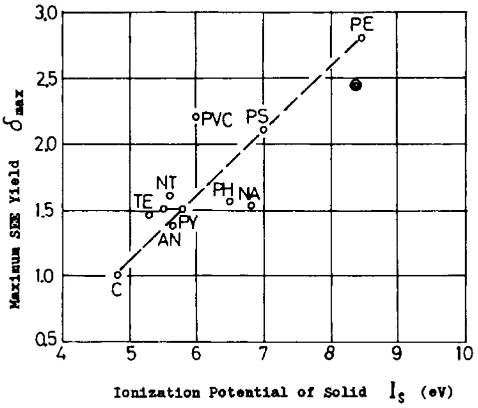


Fig. 3. Relationship between maximum SEE yield and ionization potentials of solids: (●) NaTCNQ-type FCEM.

is plausible that the compound with the high electronic conductivity shows the lower SEE yield. However, electronic conductivity is a macroscopic property which reflects the long-distance order of molecular configuration, while the SEE yield is a microscopic and statistical property which reflects the nature of the chemical bond and structure. Therefore, an organic compound which shows a low SEE yield is not necessarily electron conductive.

The data on the maximum SEE yields from organic compounds in relation to the ionization potential of solid are shown in Table II and are graphically plotted in Figure 3, where these values are ionization potentials determined by photoelectric emission from the solid. It is apparent that a high maximum SEE yield corresponds to a high ionization potential. This result is similar to the relationship between work function and maximum SEE yield for metals.[13] For a more detailed discussion of the SEE yield from organic compound, the relation of the SEE yield both to ionization potential and electron affinity would have to be considered.

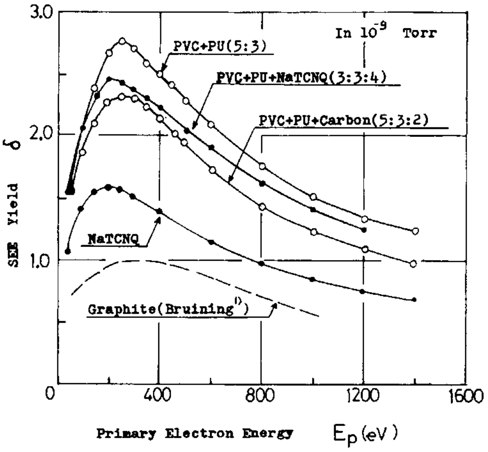


Fig. 4. SEE yields from electron-conductive polymeric compositions as function of primary electron energy.

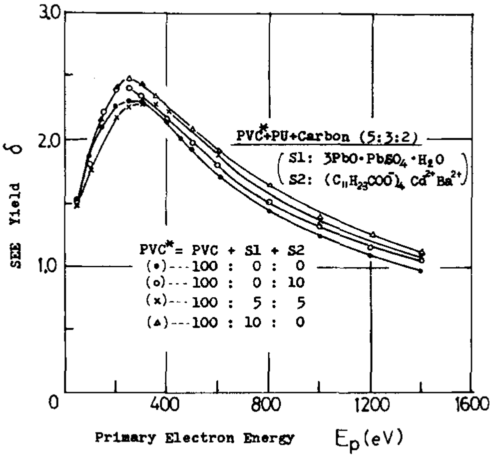


Fig. 5. Effect of stabilizers on SEE yields of polymeric compositions.

The SEE characteristics of the electron-conductive polymeric compositions applicable to the materials for FCEM are shown in Figure 4. It shows that the SEE yield depends on the characteristics of the matrix polymer, but is almost independent of the addition of electroconductive particles which inherently have low SEE yields. This fact can be understood if one assumes that the surface of the polymeric compositions becomes polymer rich by an "exudation" effect of polymer or plasticizer during the process of molding. Figure 5 shows that the SEE characteristics of the electron-conductive polymeric compositions are not affected by adding less than 5% stabilizer.

The maximum SEE yields from organic compounds are generally lower than those from inorganic insulators. However, since the values of $E_{p_{max}}$ of organic compounds are low (200–300 eV), the SEE yield in low primary electron energy regions is relatively high. This makes the application of organic polymers to CEM possible.

FLEXIBLE CHANNEL ELECTRON MULTIPLIER (FCEM)

Experimental

Some of organic polymeric compositions having an appropriate electrical resistivity of 10^6–10^{10} ohm·cm are applicable to the materials for FCEM. In this paper, three types of FCEM are made of the above-mentioned electron-conductive polymeric compositions where NaTCNQ and/or carbon black are dispersed in the plasticized PVC matrix. The sheet of the electron-conductive polymeric composition was cut into small pellets, which were then shaped into a tube through a die by the extrusion molding method. The tube obtained by this process is schematically illustrated in Figure 6 together with its dimensions. As electrode, colloidal carbon (aquadag) was first coated to both ends of the FCEM, and silver wires wound on their coated carbon were fixed by silver paint with an epoxy resin binder for obtaining low-resistance ohmic contacts.

The characteristics of the FCEM are measured in the pulse counting mode under vacuum ($<10^{-5}$ torr) by using the apparatus shown in Figure 6, where the

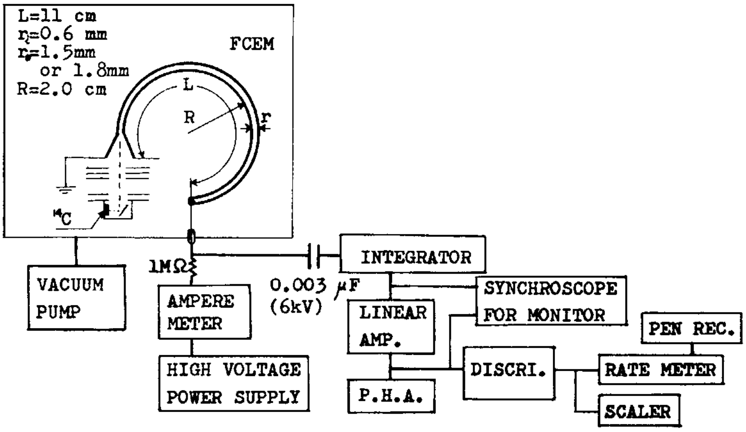


Fig. 6. Measuring system of the characteristics of FCEM.

FCEM is bent in a circular arc of radius 20 mm in order to avoid ionic feedback effect. As primary electrons for the test, secondary electrons emitted by β-ray irradiation from ^{14}C to a metal plate (Cu) were accelerated up to 300 eV and led to an input cone of the FCEM. The gain is obtained by measuring the total charge included in each output pulse. The count rate and the total counts are monitored by a rate meter and a scaler, respectively, as shown in Figure 6. This pulse counting mode is advantageous since the gain obtained is independent of the detection efficiency.

The gain G of the FCEM is given by the following equation:

$$G = \int j_0(t)dt/e = CV/e \tag{2}$$

where $j_0(t)$ is the output current at time t, C is the capacity of the condenser, and V is the peak voltage value when the condenser is charged by the output current. Mean gain $\overline{G}$ is defined as

$$\overline{G} = \sum_j G_j n_j \Big/ \sum_j n_j \tag{3}$$

where G_j and n_j are the gain and the number of pulses, respectively, in channel j of the pulse hight analyzer.

As a typical case, the electron-conductive polymeric composition is extruded through a die into a tube 10 cm in length, 1.2 mm in inner diameter, and 3.0 mm in outer diameter. A high dc voltage V_a, around 3 kV, is applied between both ends of the tube. A single electron introduced near the cathode of the tube makes hopping motions in the tube and reaches the anode. As the SEE yield of the tube material is higher than unity, the electrons at the entrance increase in number by every collision with the tube wall, and an FCEM is obtained. Under the applied voltage V_a, when the number of collisions of secondary electrons with the tube wall is n for a pass through the channel, an energy eV_a/n is imported to the secondary electrons per hopping. The SEE yield δ at the tube wall depends on the electron energy eV_a/n, and the gain G of FCEM is given by $G = \delta^n$. For a typical case, the following value of G is expected under conditions when V_a = 3 kV, n = 30, V_a/n = 100 V, and δ = 1.9:

$$G = (1.9)^{30} = 2.3 \times 10^8.$$

Results and Discussion

The size and characteristics of each FCEM made of electron-conductive polymeric composition are tabulated in Table III. The electrical resistance of the NaTCNQ-type FCEM made of PVC, PU, NaTCNQ, and stabilizers lies within the 10^{11}–10^{12} ohm range (volume resistivity $\rho = 10^9$–10^{10} ohm·cm), and its temperature coefficient has a large negative value, as shown in Figure 7. The high resistance of this FCEM is caused by the high resistivity ($\rho = 10^5$ ohm·cm) of NaTCNQ itself. However, the resistance is very stable and is independent of the thermal histories and molding conditions. In the case of the carbon-type FCEM made of PVC, PU, carbon black, and stabilizer, the resistance lies within the 10^8–10^{10} ohm range ($\rho = 10^6$–10^8 ohm·cm), and its temperature coefficient is slightly positive. Though these characteristics are suitable for FCEM, the resistance is somewhat affected by the thermal histories and molding conditions. The dispersibility of chain-structure carbon black particles in the polymer matrix may be responsible for these effects. The electrical resistance of the NaTCNQ carbon-type FCEM made of PVC, PU, NaTCNQ, carbon black, and stabilizer lies within the 10^8–10^{10} ohm range ($\rho = 10^6$–10^8 ohm·cm), and its temperature coefficient is slightly negative. This type of FCEM is excellent in the stability of its resistance, and is one of the most promising FCEM's for this development.

The voltage–current characteristics of all FCEM's are ohmic in a wide range, and the electric field strength in operation is 250–300 V/cm.

Figure 8 shows the relationship between mean gain measured and applied voltage, where a high mean gain of $\overline{G} = 10^8$ is obtained at $V_a = 3$ kV.

Figure 9 shows the count-rate dependence of the mean gain and the output current ratio I_0/I_d, where I_0 is the output current and I_d is the tube current at the time of no count. With increase in the count rate, a saturation of the output current ratio results, and the mean gain decreases. The resistance of the NaTCNQ-type FCEM is as high as 10^{11}–10^{12} ohm, and the FCEM is not adequate for high rate counting; but the output current ratio I_0/I_d reaches 10^{-1}, which would be the upper limit expected theoretically. The resistance of the carbon-type FCEM is adequately low (10^8–10^{10} ohm); but the decrease in mean gain starts at a count rate of $N_c = 10^3$ cps, as shown in Figure 9. The output current ratio tends to saturate at $I_0/I_d = 10^{-2}$–10^{-3}, which is well below the theoretical limit, and the mean gain is characterized by a gradual decrease with the increase in count rate.

TABLE III
Sizes and Characteristics of FCEM

	NaTCNQ-type FCEM	Carbon-type FCEM	NaTCNQ + Carbon type FCEM
Inner diameter, mm	1.2	1.2	1.2
Outer diameter, mm	3.0	3.6	3.6
Tube length, cm	11	11	11
Electrical resistance, ohm	10^{11}–10^{12}	10^8–10^{10}	10^8–10^{10}
Maximum output current, A	10^{-10}	10^{-7}	10^{-6}
Gain (V_a = 3 kV)		10^8	
Background		< 0.1 count/sec	

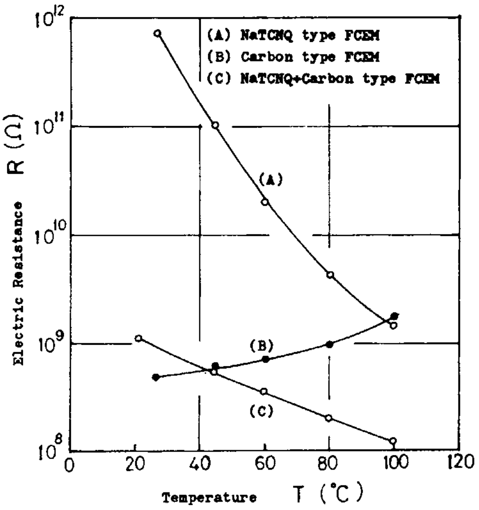


Fig. 7. Temperature dependence of electrical resistance of FCEM.

The difference in these characteristics can be attributed mainly to the charge-up effect of the high-resistance domains distributed on the inner surface of the tube, and is related to the respective electroconduction mechanisms of these FCEM materials. Because the conductivity of the FCEM materials is due to the channeling effect among electroconductive particles in the polymer matrix,

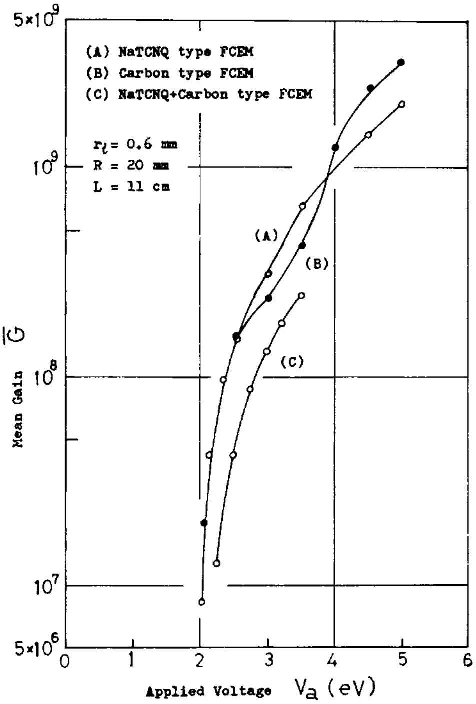


Fig. 8. Relationship between mean gain of FCEM and applied voltage.

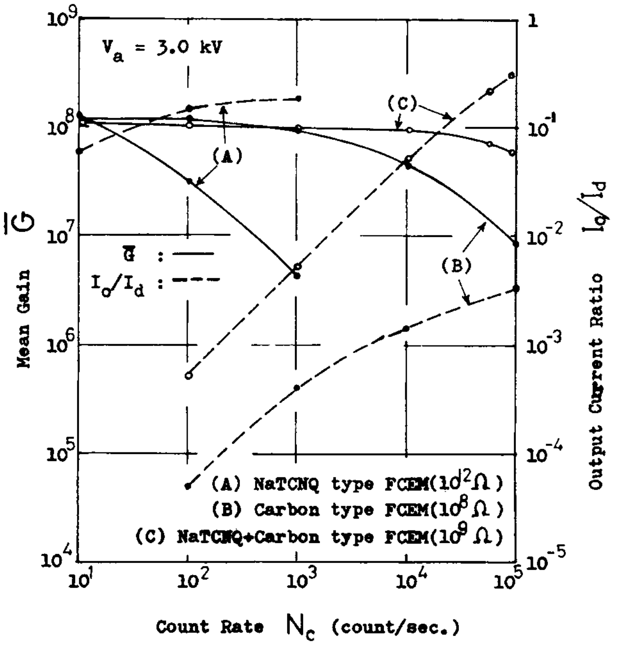


Fig. 9. Dependence of mean gain and output current ratio of FCEM on count rate.

the conductivity is determined by the quantity and dispersibility of the conductive particles. Therefore, the charge-up effect of the domains of these FCEM's is apparently based on the dispersibility of the conductive particles in the polymer matrix, where NaTCNQ has molecular dispersibility and carbon black has granular dispersibility. The NaTCNQ carbon-type FCEM, in which the dispersibility of the conductive particles is improved, shows excellent gain characteristics in a wide range of count rates, and the I_0/I_d ratio measured reaches 10^{-1} adequately.

The FCEM has also photon sensitivity in the vacuum UV region, and the UV

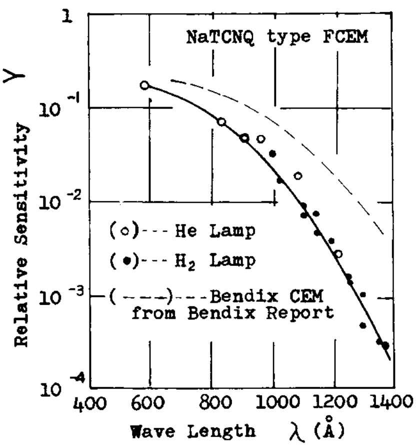


Fig. 10. Photon sensitivity of FCEM in vacuum UV region.

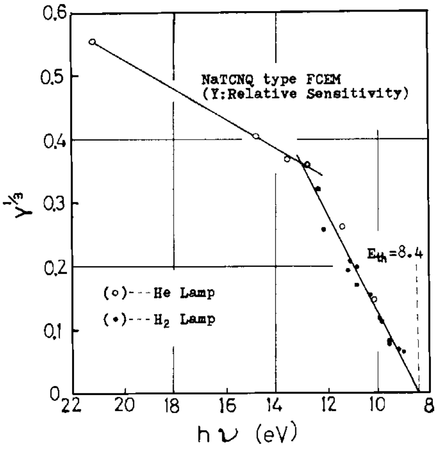


Fig. 11. Cube root plots of photon sensitivity of FCEM in vacuum UV region.

sensitivity of the NaTCNQ-type FCEM is shown in Figure 10. It is adequate for the vacuum UV photon detection. The threshold value E_{th} for photoelectric emission is given in Figure 11. This was determined by applying the cube root law,[9] where the UV sensitivity is interpreted as the quantum yield for photoelectric emission. The value of E_{th} = 8.4 eV found in the figure is taken as the ionization potential of solids, and is plotted in Figure 3 since the maximum SEE yield δ_{max} of this FCEM is 2.45, as shown in Figure 4. The plot does not show discrepancies with the general tendency of other plots.

It is confirmed that the lifetime of FCEM is 10^{10} counts in total counts, which is comparable to that of the CEM made of lead glass.[14] From this result, it is deduced that the chemical change of the FCEM materials caused by SEE would be negligibly small because of the protective effects such as the "sponge" and the "cage" effects against radiant rays.[15] Studies on the vacuum-released gases from FCEM are being carried out by the authors.

Thus, the FCEM has high flexibility, can be set in any curvature in order to avoid ionic feedback effect, and can be easily mounted in an instrument. Moreover, because of its high flexibility, the FCEM is most suitable for a space-borne electron or photon detector which is subject to considerably strong shocks and vibration. The NaTCNQ-type FCEM has already been loaded on sounding rockets of the University of Tokyo for detecting vacuum UV photon radiation in space,[16] and the carbon-type FCEM has been borne on a scientific satellite,[17] where favorable results were obtained.

The NaTCNQ carbon-type FCEM is the most promising FCEM developed recently, and shows excellent gain characteristics in a wide range of count rate. The electron-conductive polymeric composition used for this FCEM, because of its excellent molding qualities, could also be utilized as material for a channel plate whose channels are arranged. Its channel plate may be used, for example, as an image intensifier.

The authors wish to express their sincere thanks to Dr. M. Fukuda, Dr. F. Oda, and Dr. F. Nakao for helpful discussions and assistance in preparing the manuscript.

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Received June 30, 1976
Revised September 10, 1976