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RESEARCH ON LOW VOLTAGE ELECTROLUMINESCENT DEVICES WITH STORAGE

R.W. HAAS and J.M. HANLET

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By Ralph W. Haas and Jacques M. Hanlet

February 1968

Prepared under Contract No. NAS 12-545 by

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RESEARCH ON LOW VOLTAGE ELECTROLUMINESCENT DEVICES WITH STORAGE

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SUMMARY

To implement an electroluminescent display panel based upon the carrier injection phenomena, it is necessary to select an optimum material, an efficient device configuration, develop a method of fabrication that will produce the desired material properties, and investigate matrix interconnection. To initiate this program a material survey was conducted which compared general classes of materials with regard to spectral response related to band gap, type of band transition, and mobility. The survey indicated II-VI compounds as the most desirable materials. An independent study considered the various tradeoffs of various device configurations and indicated that the heterojunction approach may be desirable for the selected materials. Various methods were investigated for avoiding the formation of native atomic vacancies during vacuum deposition and a new type of evaporating heater source was designed and tested for this purpose. Finally, a small matrix of discrete EL elements was constructed and tested to confirm the feasibility of the matrix interconnection.

INTRODUCTION

This report describes the work performed under Contract NAS 12-545 for the nine month period 1 May 1967 through 29 February 1968. The primary objective was to explore techniques for generating a matrix of carrier injection electroluminescent (EL) elements, operable by low voltage and incorporating integral storage elements. The nucleus of the TMC concept is a series combination of an electroluminescent device and an avalanche diode at each matrix point. To initiate development of the above devices it was necessary to select an optimum EL material, investigate thin film fabrication techniques for these materials, and demonstrate matrix interconnection and addressing techniques. To perform these tasks a material survey was made, the first basic steps toward a successful thin film deposition were accomplished, and a small demonstration model confirmed the proposed matrix configuration.

Material Survey and Device Implementation

To survey suitable materials for implementing a matrix of carrier injection electroluminescent (EL) elements, a number of criteria can be used as a basis for selection. Certain of these criteria such as spectral match, recombination process, and mobility are directly related to the choice of material. Other parameters such as recombination volume, index of refraction, coefficient of absorption, and series resistance are criteria which govern both the choice of material, the selection of device configuration, and the fabrication process. A number of surveys which have appeared in the literature in the past decade, have mutually recognized the inherent material characteristics but naturally have been strongly influenced by the existing state of the art with regard to both device and fabrication in placing emphasis on the remaining selection criteria.

In a survey of carrier injection electroluminescent, it is certainly desirable to consider the relationship of the materials, the device structure, and the fabrication processes to the display system requirements. Desirable features for a visual display would include:

(1) A light emission that matches the spectral response of the human eye.

(2) A low operating voltage and current that minimizes the power necessary for continuous excitation.

(3) Materials and a simple device structure that permit an economical method of fabrication.

Spectral Response.- For use in a visible display, the range of possible materials that look promising for use with carrier injection can be considerably narrowed by first considering only those materials having a spectral response which provides a reasonable match to the peak wave length sensitivity of the human eye. This relationship is established by the energy gap of the material which approximately determines the maximum possible energy of the emitted photons. The response of the eye dictates the following requirements:

Visual Threshold (At Blue)	0.40 micron or 3.06 ev
Visual Maximum (At Green)	0.55 micron or 2.25 ev
Visual Threshold (At Red)	0.70 micron or 1.75 ev

Since processing of the material during fabrication can slightly alter the requirements, materials with a band gap between 1.75 electron volt and 3.6 to 4.0 electron volts might be selected for use. A review indicates that the I-V and II-V groups have an average band gap of only 1 electron volt and thus can be excluded from consideration.

As shown in Table I, the I-VII and IV-IV groups provide only a few compounds that can be classified as satisfactory. However, both the III-V and II-VI groups contain many binary compounds of sufficient band gap.

GENERAL GROUP	MATERIAL	BAND GAP	GENERAL GROUP	MATERIAL	BAND GAP
I - VII	CuBr	2.9	III - V	BN	-
	AgI	2.8		AlN	5
				AlP	2.5
II - VI	CaS	5.4		AlAs	2.4
	CaSe	5.0		AlSb	1.5
	CaTe	4.3		GaN	3.4
	MgSe	5.6		GaP	2.24
	MgTe	4.7		GaAs	1.4
	ZnO	3.2		GaSb	0.67
	ZnS	3.7		InP	1.25
	ZnSe	2.6		InAs	0.33
	ZnTe	2.1		InSb	0.18
	SrO	5.8		BP	5.0
	SrS	4.8			
	SrSe	4.6			
	SrTe	4.0	IV - IV	SiC	2.3 (Cubic)
	CdS	2.4			2.9 (Hex)
	CdSe	1.7			
	CdTe	1.5			
	BaO	4.2			
	BaS	4.0			
	BaSe	3.7			
	BaTe	3.4			
	HgS	2.0			
	HgSe	0.6			
	HgTe	0.02			

TABLE I

BAND GAP COMPARISON

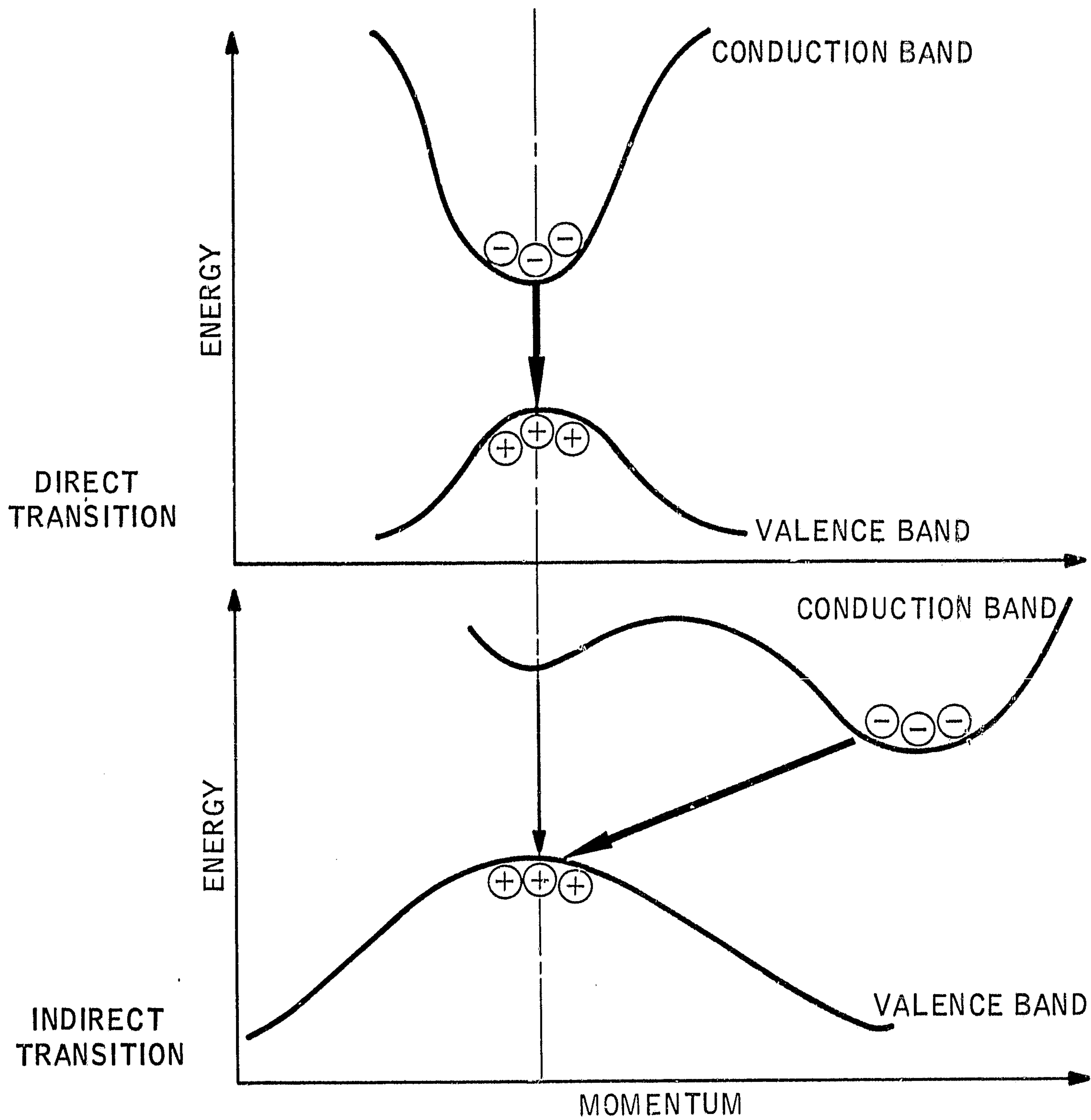
Photon Generation.- The mechanism of carrier injection electroluminescence is based on the phenomena of an excited semiconductor returning to a state of equilibrium concentration of holes and electrons by means of recombination transitions which produce light. These transitions involve the recombinations of electrons and holes accompanied by the emission of photons. Other recombination processes which are non-radiative, must be suppressed or minimized. A transition which takes place between a minimum in the conduction band and a maximum in the valence band is called a direct transition if it does not involve a change in direction of motion of the electron and hole. For this condition, both the electron and hole must have the same momentum, the transition can occur directly with the emission of a photon, and both energy and momentum are conserved. However, if the above minimum and maximum do not occur for the same direction of motion, an indirect transition will be the result of the recombination. The lowest energy conduction electron will have a momentum that is different from the momentum of the hole in the valence band, and a phonon is emitted to conserve momentum, thus producing heat instead of light. In an indirect transition, a recombination can occur with the electron and hole having the same momentum resulting in a radiative recombination but this case is statistically less likely to happen. With direct transitions, the rate of recombination is both fast and competitive with other recombination processes resulting in a high internal quantum efficiency. Indirect transitions have much slower recombination rates with an attendant lower internal quantum efficiency. (Figure 1)

A higher current density is necessary to increase the probabilities of occurrence of radiative recombinations and the production of useful light in materials that exhibit indirect transitions which are likely to produce non-radiative recombinations. The two factors, low internal quantum efficiency and high operating current make these materials poor candidates for use in visual displays.

Table II shows a listing of materials that meet the spectral response requirements discussed above and indicates the type of transition. Aluminum Phosphide has not been listed since it is chemically unstable. Copper Bromide and Silver Iodide have been deleted since both are purely ionic crystals.

It can be seen that, in general, the III-V compounds exhibit an indirect type of transition while the II-VI compounds provide a direct transition which permits a higher internal efficiency. Of the II-VI compounds, ZnSe, ZnTe, and CdS most closely match the peak of the visual region. (2.25 ev) In addition, these materials have a relatively high value of mobility. Since the requirements for high conductivity in a material are related to carrier mobility and depth of donors and acceptors, this becomes a very desirable property.

Device Configuration.- The selection of a device structure to provide the necessary excitation is just as important as the selection of a material based on the spectral response, efficiency and other factors. At least three basic methods will be discussed, the injection of electrons into a p region where a large concentration of holes exist, the injection of holes into an n region where a large concentration of electrons exist, or the injection of both electrons and holes into an insulating region. Normally, a p-n junction is used to



TYPES OF BAND TRANSITIONS

GROUP	MATERIAL	BAND GAP	TYPE TRANSITION	MOBILITY	
				ELECTRON	HOLE
II - VI	ZnO	3.2	Direct	180	
	ZnS	3.7		110-140	
	ZnSe	2.6	Direct	100-530	
	ZnTe	2.1	Direct		425-1000
	CdS	2.4	Direct	200	15
	BaSe	3.7	Direct		
	BaTe	3.4	Direct		
	HgS	2.0	Direct		
III - V	AlAs	2.4	Indirect	1200	200
	GaN	3.4			
	GaP	2.24	Indirect	80	100

TABLE II

TRANSITION COMPARISON

accomplish the first two methods and a form of p-i-n structure permits the implementation of the third method.

If an n-type material is placed in contact with a p-type material, a junction is formed. Initially, electrons will tend to diffuse from the n-type into the p region and holes will diffuse from the p-type material into the n region. The removal of electrons from the donor sites in the n-type material provides a collection of positively charged donor ions. Similarly, the flow of holes from the acceptor sites leaves a number of negatively charged acceptor ions in the p region. This condition will cause an electrostatic layer to be formed at the junction with an electric field whose polarity will oppose the current flow. The magnitude of this potential will be determined by the position of the Fermi level in the n-type and p-type materials. As described above, the position of the level in each region will be determined by the concentration of the impurity incorporation by doping and the temperature.

If an external potential is applied to the junction with a polarity such that the height of the barrier is reduced, the junction is said to be forward biased. A large hole current will flow from the p region to the n region and a large and equal electron current will flow from the n region to the p region. If, however, the n region is very heavily doped and the p region lightly doped, a condition of minority carrier injection will occur. The junction current will be carried mainly by electrons and large excess electron concentrations will be injected into the p region. These carriers will diffuse approximately one diffusion length away from the junction and recombine. For opposite conditions of doping, hole injection into the n region is possible. The selection of the type of minority carrier injection is usually based on the material, since in many compounds one carrier will exhibit a much higher mobility.

Another implementation for carrier injection can be provided by placing a metal in contact with an n-type material. It is then possible to inject holes under a condition of forward bias similar to the p-n junction mechanism. The efficiency is low since the injection current represents only a part of the total current.

A tunneling injection technique is possible by using an insulating film in contact with a semiconductor material. This approach requires a high voltage drop across the insulator.

Another form of junction has been used for injection with those materials that tend to form unipolar extrinsic conduction states. Some materials are strongly n-type and others are strongly p-type and resist changing from this type of conductivity even with heavy impurity doping. For example, ZnTe has a tendency to remain p-type while ZnSe has a tendency to remain n-type. If the two materials are used to form junctions called heterojunctions, these junctions will behave similar to a simple p-n junction.

The recombination of an electron and a hole can never produce more than one photon, thus the internal quantum efficiency discussed above can never exceed a value of one. A most important criteria for a carrier injection device is the external quantum efficiency

which relates the number of photons produced at the surface of the device and the current required to produce these photons during operation. This measure of efficiency accounts for losses in the device due to absorption and transmission, in addition to internal quantum efficiency. The ratio of photons emitted to photons created will certainly depend on the critical angle beyond which the light is internally reflected. The light emerging from the junction is limited to the photons emitted in a direction within a small cone of aperture which is defined as a function of the index of refraction. Within this angle light will still be submitted to reflectivity at the interface and reduced by this factor. For example, in a material with an index of refraction of 3, 25% of the light will be reflected. 55% of the light will be reflected in a material with an index of 6.7. In addition to this loss, photons may be destroyed by free carrier absorption. It can be shown that the absorption coefficient is directly proportional to the carrier density and the square of the wavelength. These device parameters place an additional burden on the material by requiring a low index of refraction or a more complex structure of the junction to cope with highly refractive materials.

Certain problems dominate for each method of injection discussed above, whether the device implementation is a simple p-n junction, a heterojunction, or a hybrid configuration such as a p-i-n structure.

If the semiconductor material is amphoteric, or can be made n-type or p-type, abrupt p-n junctions can be made from now familiar technologies. With the direct transition materials, a high internal efficiency can be expected. The major problem pertaining to this structure is the photon extraction from inside the junction in order to achieve an equally high external efficiency.

The problem with the heterojunction approach is that of finding another semiconductor of opposite conductivity type with equal band gap, having an identical lattice constant, similar coefficient of expansion, and similar growth habits. If this condition is met, the internal efficiency can be comparable to that of the p-n junction. The fact that the electroding must be made purely ohmic for both electron and hole injection poses another requirement of suitable work function for the electrodes.

With the p i n junction structure, the problem is that of material compatibility. A high degree of physical and chemical compatibility must be exhibited by the five material layers that form the device; the thin layer of intrinsic material in which the recombination occurs, the wide band gap material of low work function and the wide band gap material of high work function that are deposited on either side of the intrinsic layer, and the outer injecting electrodes. (One must be transparent.) The lattice and band gap requirements are somewhat relaxed with this approach as compared to those mentioned in the previous structures. However, the requirements for similar coefficients of expansion and a high conductivity in the transparent conductor are quite stringent.

In all of the structures mentioned above, a high current requires high mobilities, a low forward resistance, and a junction width that is shorter than the diffusion length of the carriers. The diffusion is controlled by the carrier lifetime which depends upon the various capture and recombination processes.

Material Structure Considerations

Since no simple element can satisfy the desired band gap requirements, with the exception of diamond, the choice of a host crystal material is limited to compounds. The most likely candidate seem to be from the II-VI group of elements. These compounds, by Goldschmidt's rule, which determines lattice organization as a function of atomic radii, crystallize in the blende or wurtzite structures; specific forms, in space, of repetitive patterns of lattice structural cells. It can be inferred from Welker's rule, which defines the degree of ionicity in the atomic band, that these partially ionic high bond strength material should provide high mobilities with small scattering of the mobile carriers.

However, as they chemically form, all II-VI compounds have a tendency to form vacancies, or point defects resulting from missing atoms in the lattice structure, and have a tendency to form various spatial arrangements of the atoms forming the elementary lattice cells. The vacancies are formed due to the polymeric form assumed by the chalcogene, or an element that is listed in Column VI of the periodic table, and result in low conductivity. The mixtures of crystalline structure occur in spite of the fact that the length of the atomic bonds remain unchanged and the differences in structure appear only when other than first nearest neighbor atoms are considered. The differences result in complex scattering modes between optical and acoustical vibrations in the lattice. A combination of these vibration modes can produce an undesirable shift in band gap and a lower mobility due to an increase in the effective mass of the carrier.

Both defects, vacancies and structures, are strongly dependent on the processing temperature, because, as they are heated, the compounds dissociate into elements of dissimilar vapor pressures. The effects of the temperature, however, vary in opposite directions with respect to vacancies and structures. For example, at moderate temperature of preparation, the chalcogenes do not appear in a monoatomic form, and hardly at all even as diatomic specie, but mainly as molecules of 4, 6, or 8 atoms. On the other hand, the crystalline orientation preferentially assumes only the blende structure, which presents a single mode of optical or high frequency of vibration from its spatial arrangement. Whereas, at high temperature, the contribution from diatomic molecules increases, though not to the extent of excluding puckered rings of 6 to 8 chalcogene atoms. The structure assumes then an hexagonal packing and, as a consequence, it has an acoustical mode or low frequency of vibration ensuing from its spatial arrangement of atoms.

The problem of polymerism is about the same for any chalcogene; however, the one of structure is mostly one of degree, i.e., the extremes of the vertical series of the periodic tables assume only one crystalline form, varying from hexagonal Zincite for the oxygen compounds to cubic Sphalerite for the telluride compounds.

Besides the polymerism, responsible for the vacancies formation, the atomic sizes of the constituent elements define the levels where native donors and acceptors will be found in the gap, as well as the type of conductivity these native defects will produce. Hence, the increasing size of the group II elements will promote negative conductivity whereas

elements from the group VI will give opposite results: in other words, going down the Column II, from beryllium to mercury, with the atomic diameter increasing from 2.25 Å to 3.10Å will secure an n-type conductivity; conversely, going down the column VI from oxygen to tellurium, with the atomic diameter increasing from 1.32 Å to 2.9 Å will secure a p-type conductivity.

With respect to the location of the various levels in the band donor or acceptor of native origin, it can be said that the biggest of the two atoms in a band will always be located close to the band to which it belongs when a vacancy of the other atom occurs. Hence, since the metallic element is associated with the conduction band and the non-metallic one with the valence when, for example, in CdS a sulfur vacancy occurs the excess cadmium atom will be located close to the conduction band, where it may easily ionize and contribute to the conduction. In ZnTe, if a tellurium vacancy is produced the excess zinc atom of smaller radius will be located far below the conduction band and contribute nothing to the conductivity.

Conversely, if cadmium or zinc vacancies occur, the sulfur atom in excess will be high above the valence band so high as to be unable to contribute to hole conduction, whereas the much bigger tellurium atom would be close enough to the valence band to be easily ionized and give hole conductivity. This follows from the cation/anion radii ratio which takes a value greater than unity for CdS and smaller than unity for ZnTe; this ratio therefore gives an indication on the compensation tendency in these II-VI compounds. This compensation depends on the energy gained in a transition of electron from donor to acceptor. This gain in energy can be considered high only when both are shallow in which case the energy gained by the transition may exceed the energy needed to form the vacancy.

Since compensation between vacancies means electrical neutralization, this should be prevented by proper doping; this is possible when the cation and anion have equally deep ionization levels and an adequate solubility, i.e., when they can be introduced into the host crystal at the desired concentration.

Numerous studies have shown that incorporation of Group III elements in substitution for Group VI provides n-type conductivity, and Group V elements in substitution for Group VI provides p-type conductivity in II-VI compounds, although sufficient concentration has not been achieved equally well for p and n dopants. Thus, the carrier concentration achieved by impurity incorporation is still somewhat short of its goals and there is limited hope in that direction.

A great amount of work in industry has shown that carrier injection can be excited in many materials with a wide range of device structures. The only decent efficiencies have been achieved with the II-V compounds such as GaAs which can emit in the visible red. The following efforts, however, are representative of efficiencies achieved in the visible region:

(1) External quantum efficiencies of 2% were obtained with injection through an

insulating film into P doped ZnTe at 5340 A with the temperature at 77°K.

(2) With a metal-insulator-p-type tunnel diode of ZnTe, an efficiency of .01% was observed at 5375 A and 77°K.

(3) With an avalanche structure, an external efficiency of 2% at 5380 A and 77°K was observed with P doped ZnTe.

(4) An 18% external quantum efficiency was obtained from p-n junctions at 70°K with a 6300 A emission in $ZnSe_xTe_{1-x}$.

In summary, on the basis of spectral response and internal efficiency, the II-VI compounds appear most desirable for use as carrier injection host crystal materials. ZnSe, ZnTe, and CdS most closely match the peak of visual sensitivity. From a structure standpoint, the most encouraging results to date have been achieved with the heterojunction structure. It is believed that with a more efficient technique in preparing the materials and in producing junctions, a combination of II-VI compounds can be considered to be the most promising to give efficient electroluminescence at room temperature.

Material Development

The processing planned for the II-VI compounds consists of two basic steps: (1) the deposition of an amorphous host crystal by coevaporation and (2) the recrystallization of this deposition by a scanning electron or ion beam in an ultra high vacuum station. These efforts are discussed below.

In DC electroluminescence, the criterion for an efficient injection mechanism resides in an efficient radiative recombination process. The efficiency is lowered by radiationless recombinations that result due to the fact that vacancies which can be compensated tend to form electrically neutral pairs. The ability to avoid formation of native vacancies is the first prerequisite in considering the selection of a compound of suitable band gap for the visible region.

Defects caused by vacancies which are inherent in chalcogenides may originate from different causes: first, during production of the compound, the chalcogene may assume a polymeric form inactive in the mass action equilibrium and the higher molecular state which prevents diffusion in the lattice; second, the crystallizing compound, even when stoichiometrically perfect, may still assume more than one steric coupling and thereby exhibit several scattering modes; third, the ability to form neutral pairs increases with the amount of ionic bonding in the crystal.

In order to prevent the large concentration of Zn vacancies that would result from the dissociation of ZnTe during evaporation of the compound, a new type of evaporating source has been designed to evaporate the individual elements simultaneously and satisfy stoichio-

metry and mass action laws during the gaseous phase. This source must not only provide separate control over the equilibrium constant of each element evaporated but also obtain their equal distribution on the substrate.

The rate of effusion, from kinetic theory is given by

$$n_o = \frac{P_s}{(2\pi RMT)^{1/2}}$$

and the number of emitted molecules landing on the substrate is

$$n_{o/o} = n_o \exp h/\lambda$$

where, P_s is the vapor pressure at the temperature T obtained from Gibbs' law; with M, the molecular weight, and R, the gas constant per mole, h the distance substrate-source and λ, the mean free path.

$$\lambda = \left(\frac{0.707K}{\pi \ \delta^2}\right) \left(\frac{T}{P_s}\right)$$

with k, Baltzmann's constant and δ , the diameter of evaporating atoms or molecules,

$$\delta = 1.32 \times 10^{-8} \left(\frac{M}{e}\right)^{1/3}$$

The distribution along an axis, x, originating from a point directly above the source will vary according to the source configuration, i.e., the Knudsen's point source or the Langmuir's evaporating surface, hence, for a point source

$$N_p = \left(\frac{n}{2\pi\rho h^2}\right) \left[1 + (\frac{x}{h})^2\right]^{-2} \qquad \text{point source}$$

and

$$N_s = \left(\frac{n}{\pi \rho h^2}\right) \left[1 + (\frac{x}{h})^2\right]^{-2} \qquad \text{surface source}$$

In order to secure the same concentration as a function of the angle of incidence of Zn and Te at any point x, the two sources must have exactly the same origin, which obviously precludes the use of surface source which can only be used side by side.

To satisfy concentration and thickness uniformities over large x values, the evaporator conceived for this task consists of two circular and concentric sources which have a common orifice of evaporation. They are individually heated by radiation. See Figure 2.

With this geometry for the source, which presents a common and circular orifice of evaporation, the contribution to the coating at a point x, from a length of evaporation RdB will be proportional to

$$\frac{R d\beta \,\mathrm{Cos}\, x}{D^2}$$

with

$$\mathrm{Cos}\, x = \frac{h}{D}$$

and

$$D = (x^2 + R^2 + h^2 - 2\, x\, R \cos\beta)^{1/2}$$

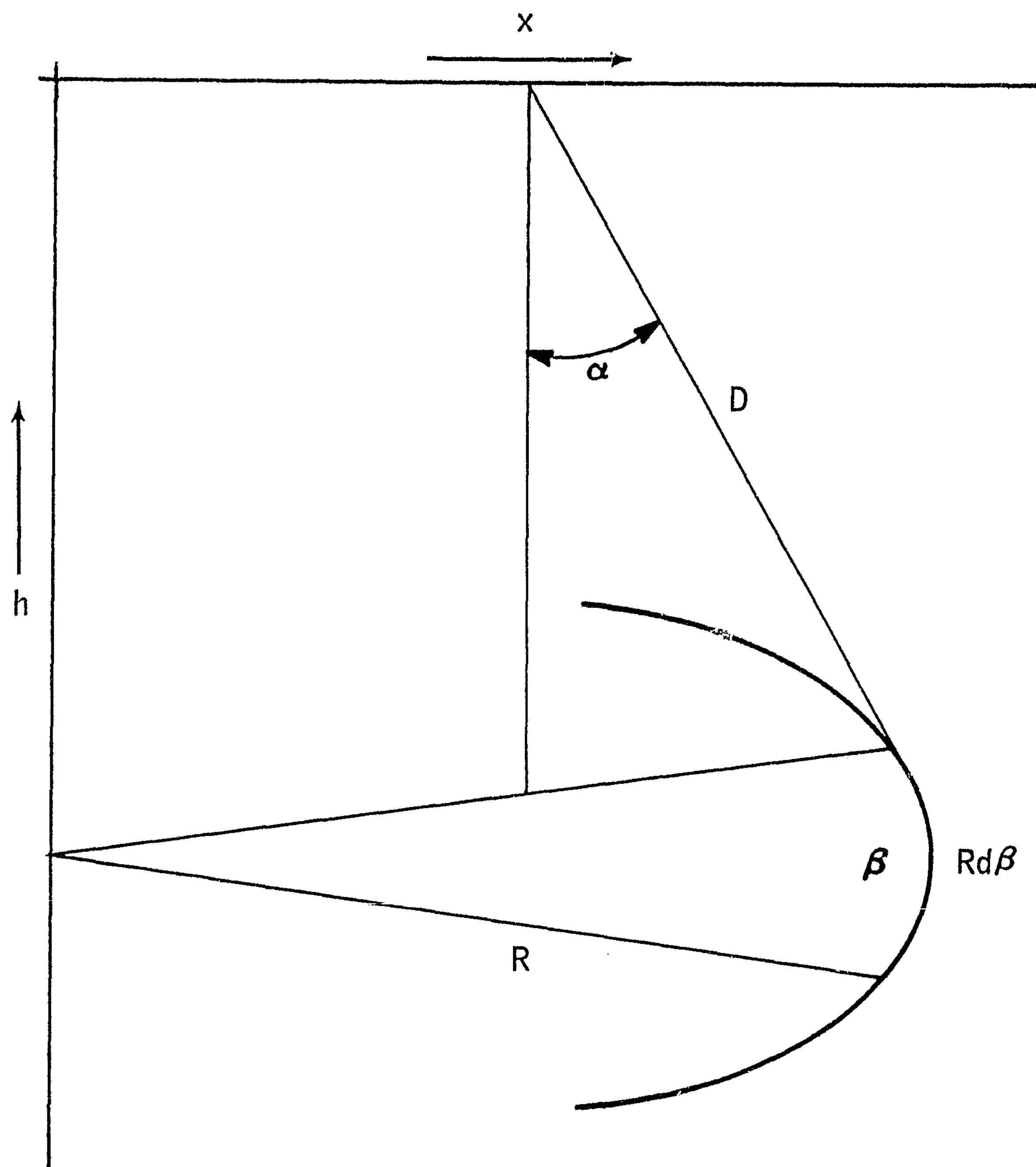
the coating at x can then be expressed by

$$\int_{\delta}^{\pi} (x^2 + R^2 + h^2 - 2\, x\, R \cos\beta)^{-3/2} \, d\beta$$

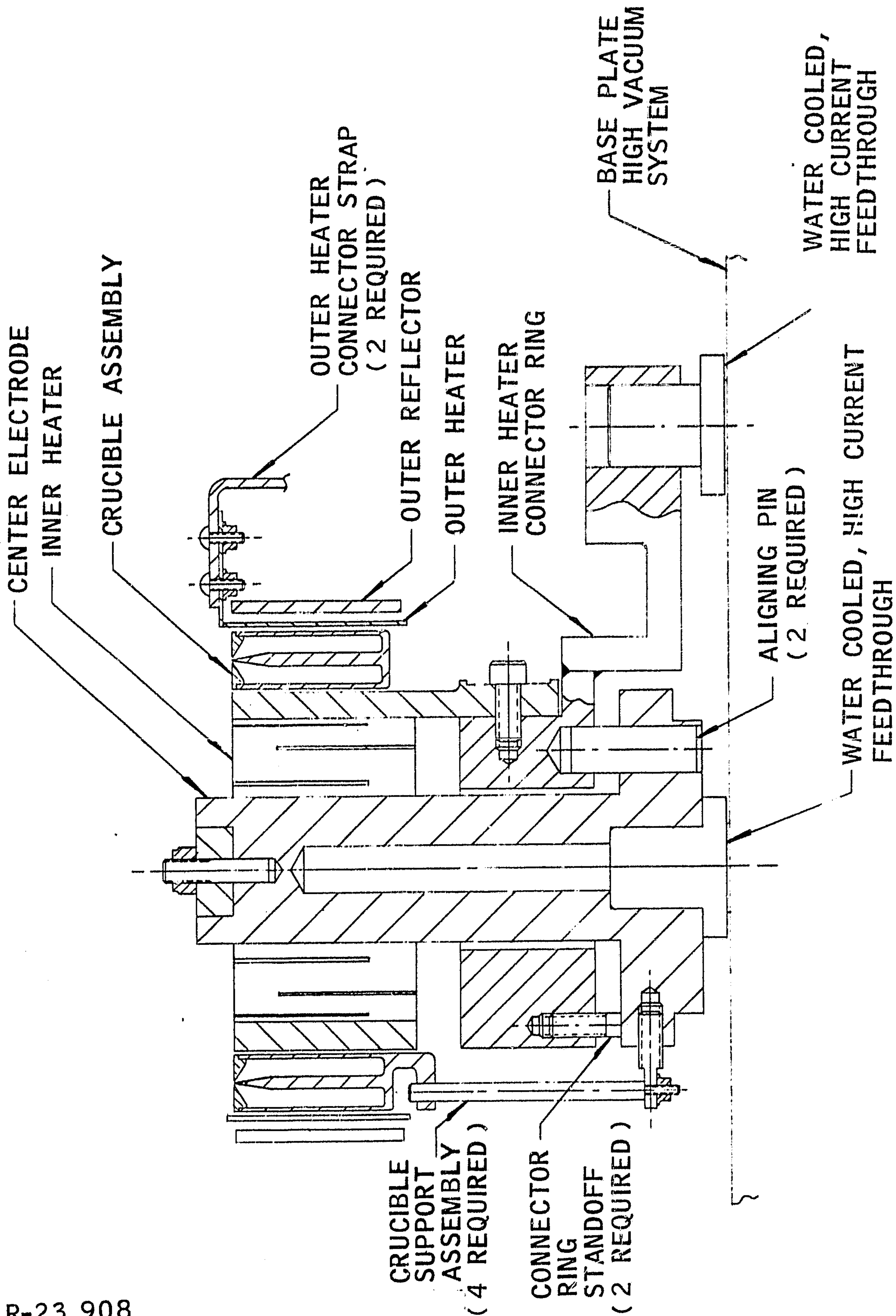
which after expansion in powers of CosB and integration, gives a series whose terms can be expanded in powers of x. The variation in coating as a function of x can then be obtained in terms of h and R only.

This special heater source (Figure 3) has been constructed and tested which shows that a satisfactory temperature gradient exists between the two sources, permitting thereby the independent control of the vapor pressure of Zn and Te and/or Se, within the limits requested by the condensation mechanism. (See Figures 4 and 5)

In order to secure the vapor of the chalcogene in monomeric form, the large molecules of Te_2, Te_4, etc. and Se_2, Se_4, etc., which assume such form because the element is



SOURCE GEOMETRY

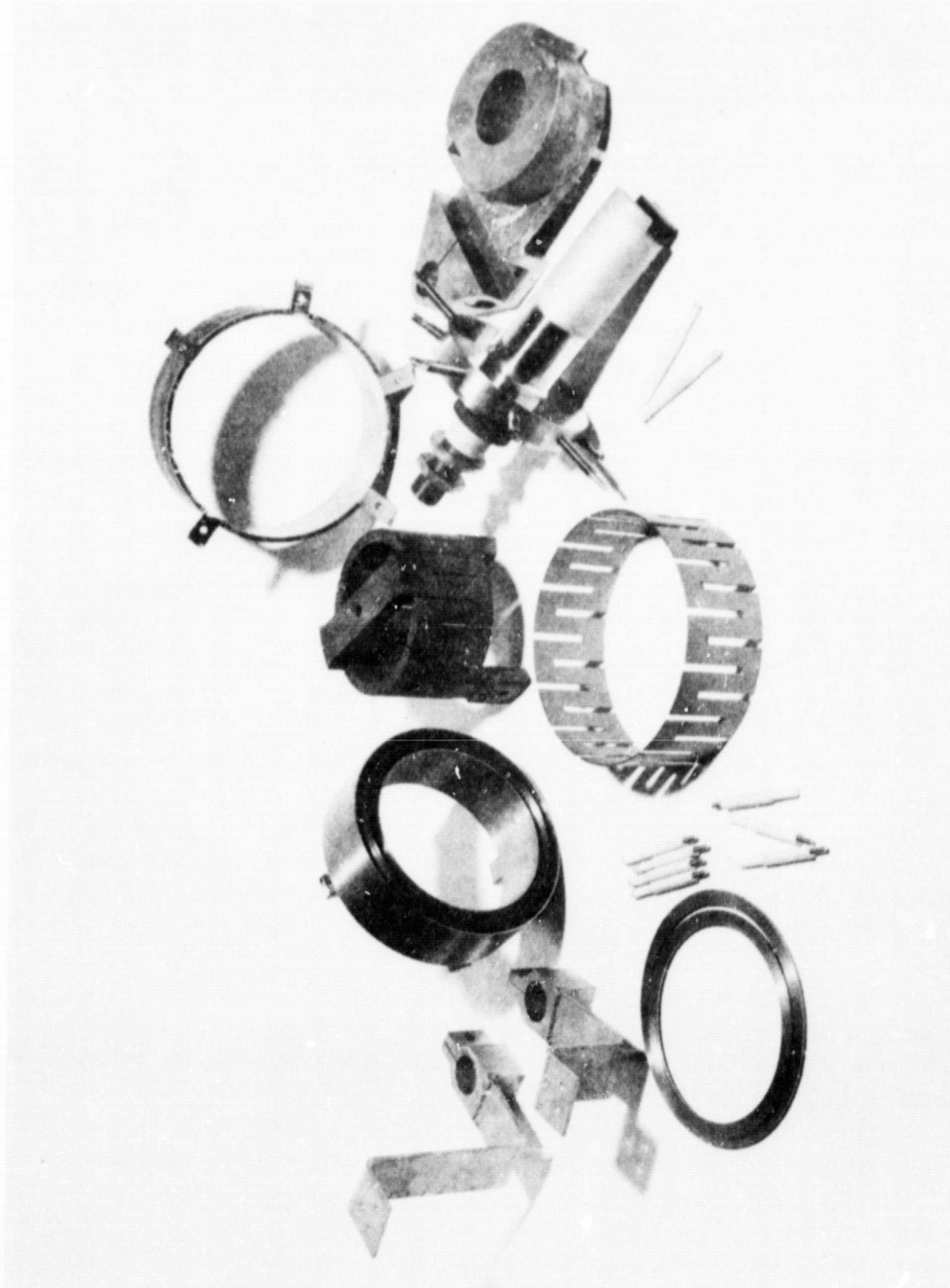


EVAPORATION HEATER SOURCE

R-23,908

Figure 3

ASSEMBLED EVAPORATOR SOURCE CONFIGURATION



COMPONENTS OF EVAPORATOR SOURCE CONFIGURATION

R-23,910
Neg. 8716-2

Figure 5

evaporated at low temperature, are dissociated with their monomer Te or Se, by heating the emerging vapor at a temperature higher than 2500°K. To do so, a filament heater was mounted on the cover of the Knudsen source, its location being determined as a function of the molecules mean free path. As an average the temperature of this filament is approximately 2000°K higher than the melt itself. As the vapor stream leaves the source, it is essentially monoatomic as revealed by mass spectrometric measurements.

However, because of the large difference in temperature of the two monoatomic gases, namely Zn and Te, the rate of condensation is unequal and therefore stoichiometry is impaired unless a suitably low temperature is maintained at the condensing surface to provide the same rate of adsorption as of evaporation. In such case, epitaxy is hardly achievable since the mobility of the condensing atoms is highly reduced. This is true whether calcium compounds, or germanium, is used as a substrate, though either one would otherwise be satisfactory on structural or mechanical grounds. These other means of crystallization had to be investigated.

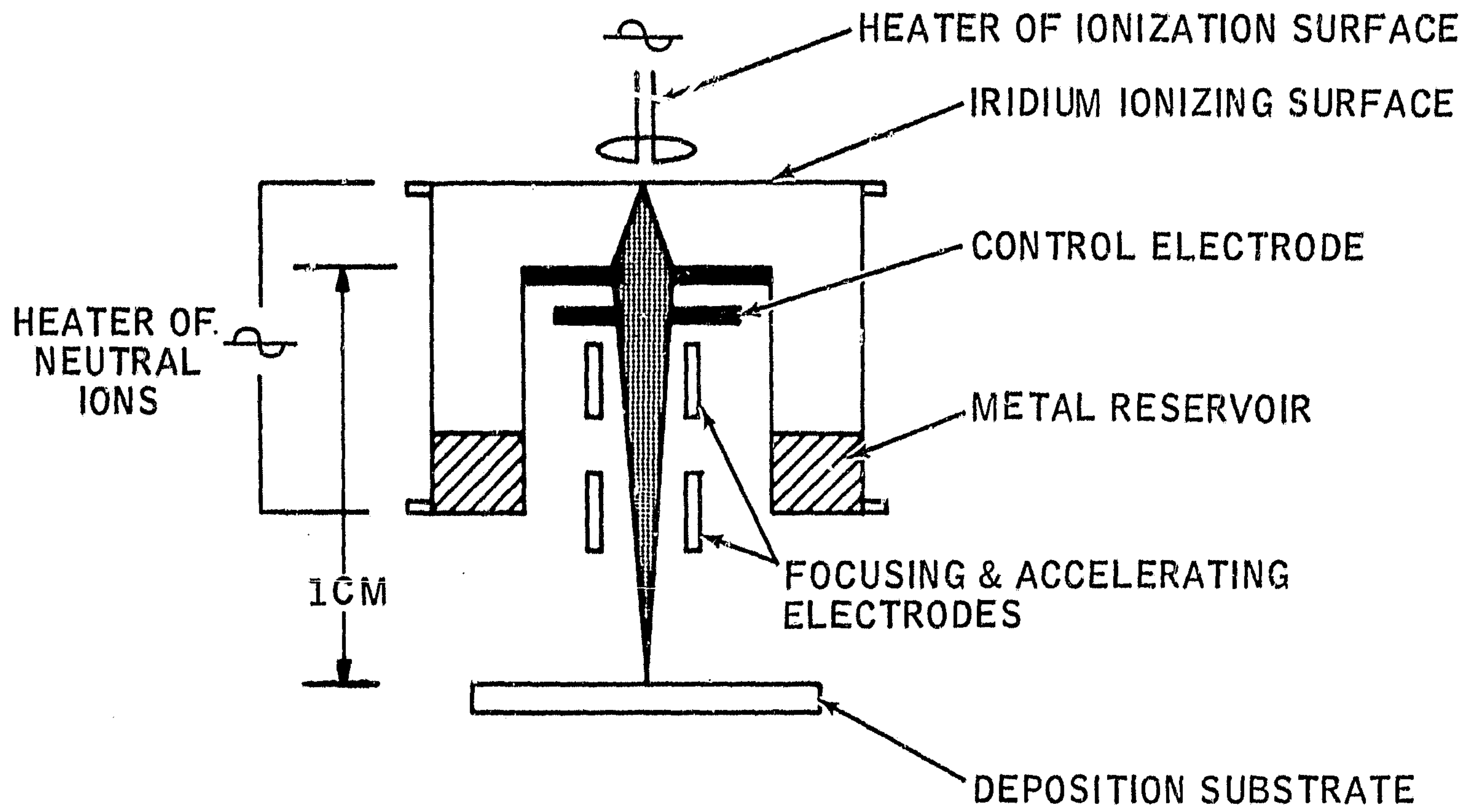
After a perfectly stoichiometric condensate of Zn and Te and/or Se has been obtained, recrystallization is secured by controlling the surface tension of the film by localized heating, in other words by zone melting of the film and seeding.

Provision must be made to account for re-evaporation from the substrate during crystallization. This condition is satisfied by providing kinetic energy to ions of the same specie as the evaporating atoms. The film is heated by bombardment with Zn atoms. This molecular beam source developed during other programs is represented in schematic form in Figure 6 The components and semi-assembly are shown in Figure 7 and Figure 8. The complete system comprised of the fuel reservoir (Zn) electro optic elements, ionizing iridium surface and its electron beam heater, is shown in Figure 9.
The heat liberated by the impinging atoms of zinc suitably focussed is sufficient to melt the film locally in an area smaller than a micron. As the beam is displaced the zone melted crystallizes and the growth can proceed over the entire film area by displacement of this hot zone, by a mechanism akin to the well known Bridgman's technique.

The motion can be produced by electrical or mechanical means, in the first case, by electrostatic or electromagnetic fields, although the scanned area is very limited due to field distortion. In the second case, the substrate is moved relative to the ion beam by a precision scanning fixture, visible in Figure 10 and Figure 11.

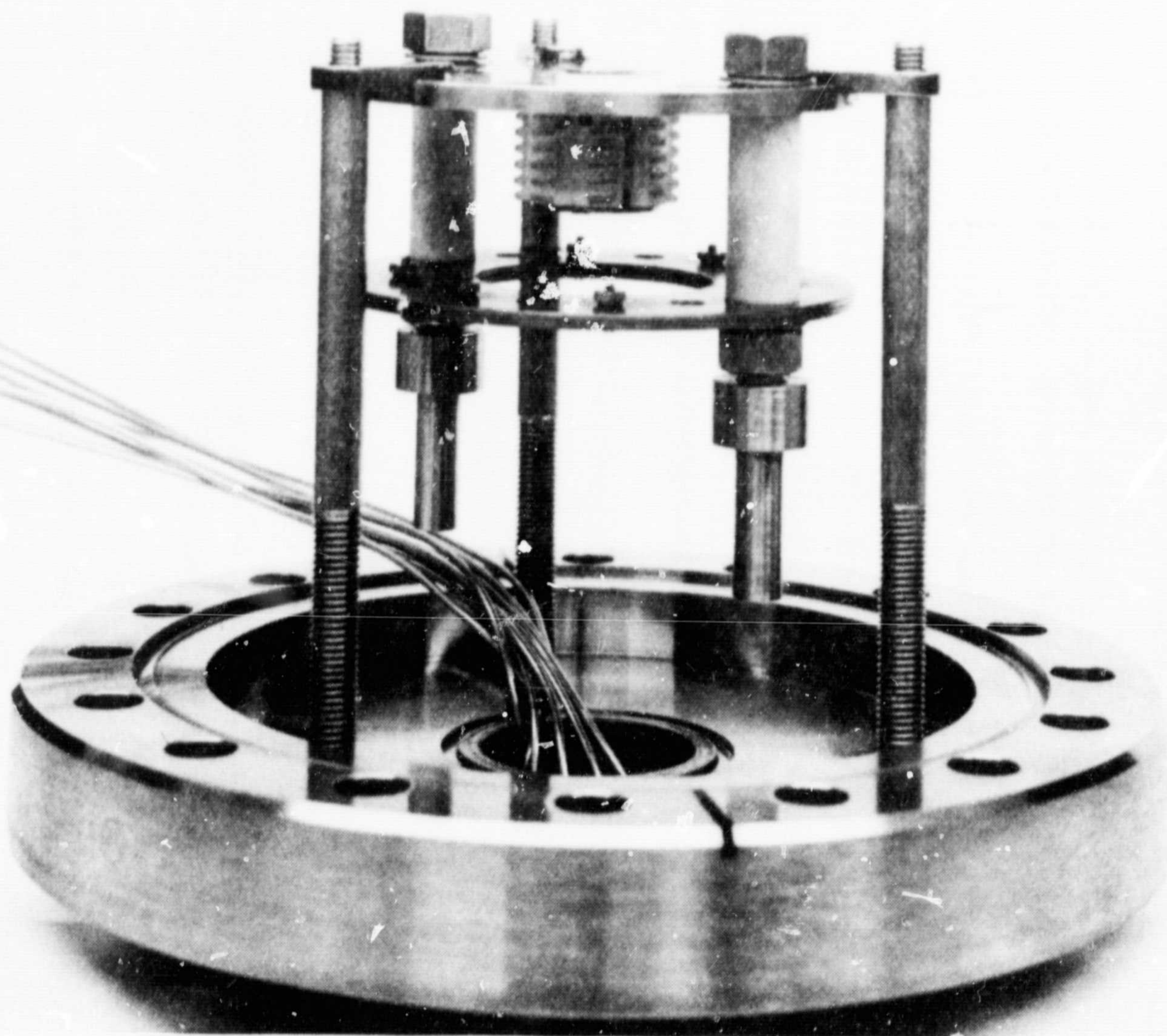
A design study was conducted to produce a fixture which will provide this precise motion by using 2 Varian linear motion feedthroughs into the vacuum chamber. Maximum travel of the substrate carrier will be 1 inch with an accuracy of 10 microinches. Scanning ("Y" direction) and indexing ("X" direction) velocities will be constant at 3.9 mils per second. Scanning can be performed at an operating temperature of 300° - 350°C.

To accurately determine the beam diameter of the ion gun used for seeding and recrystallization of the evaporated ZnTe layer, a movable table with a wedge mounted on top



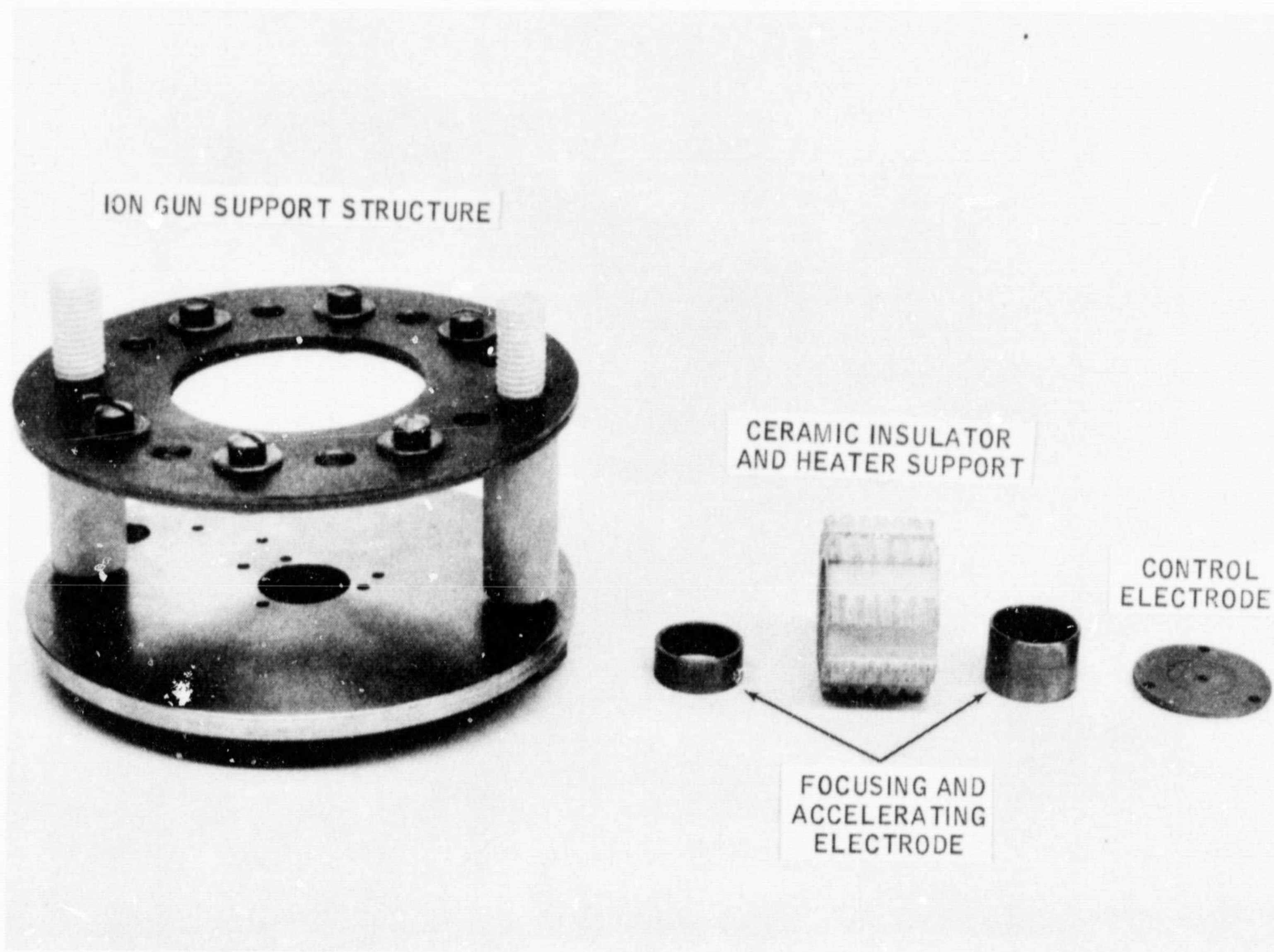
ION BEAM DEPOSITION

Figure 6

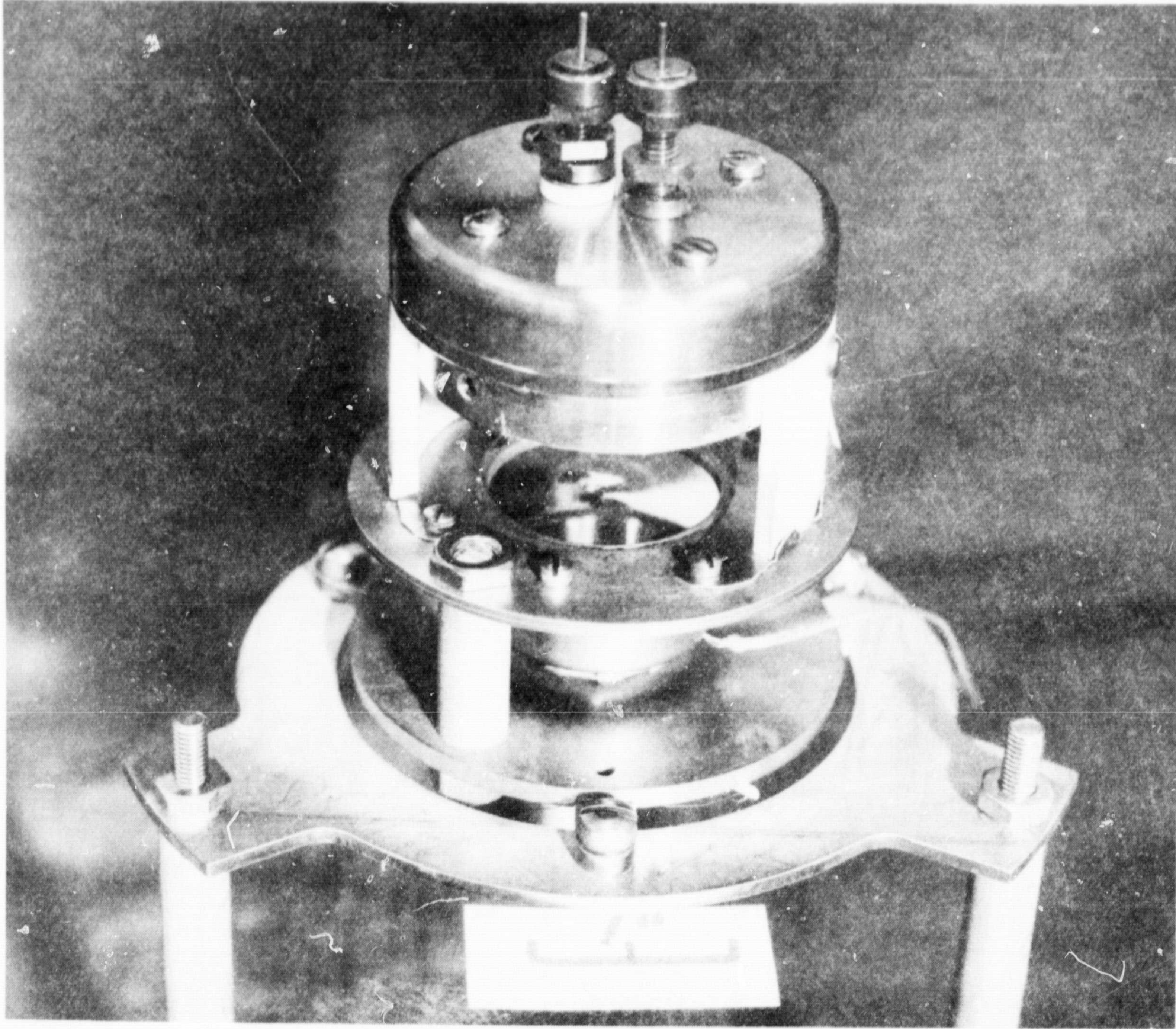


ION IMPLANTATION GUN
FUEL RESERVOIR REMOVED

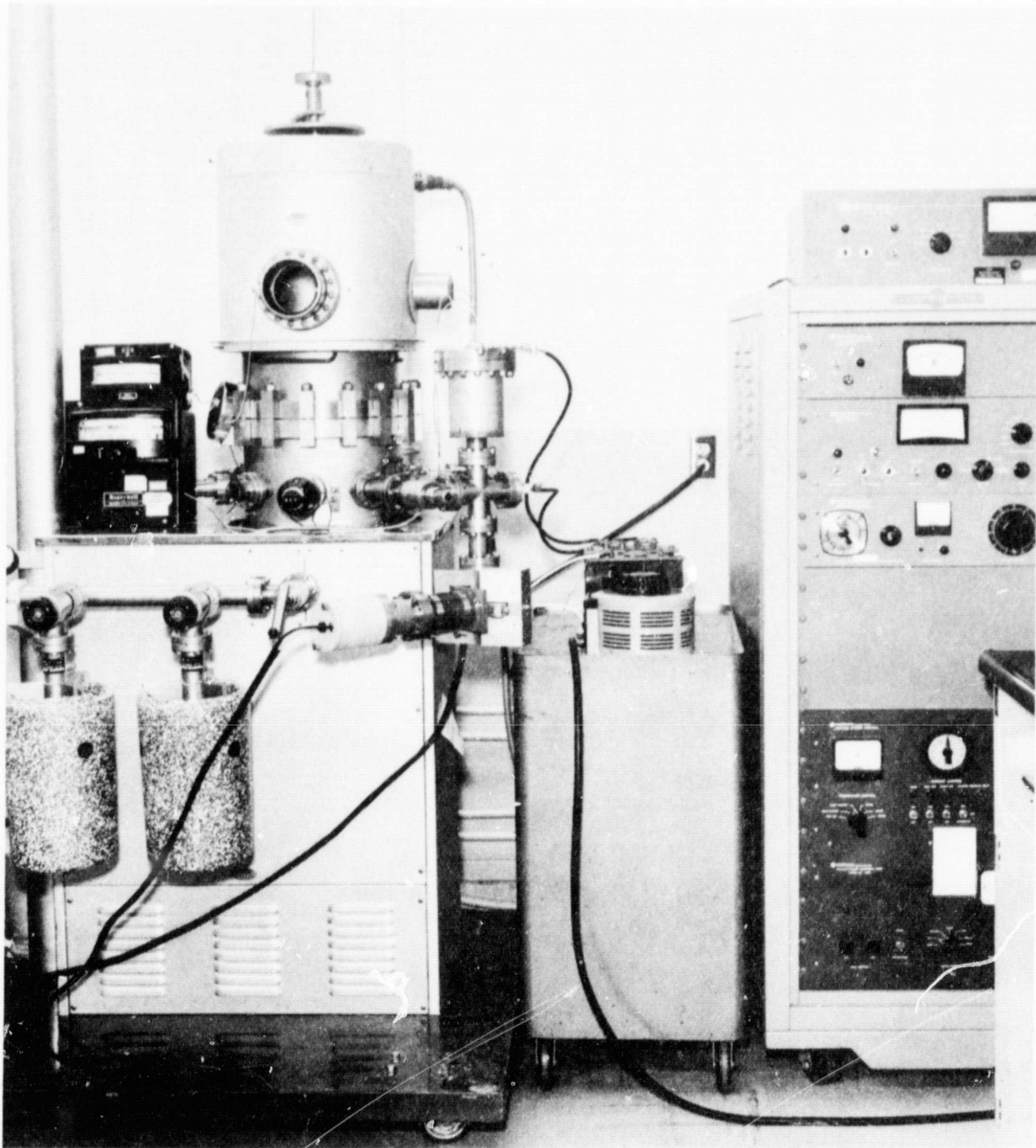
Figure 7



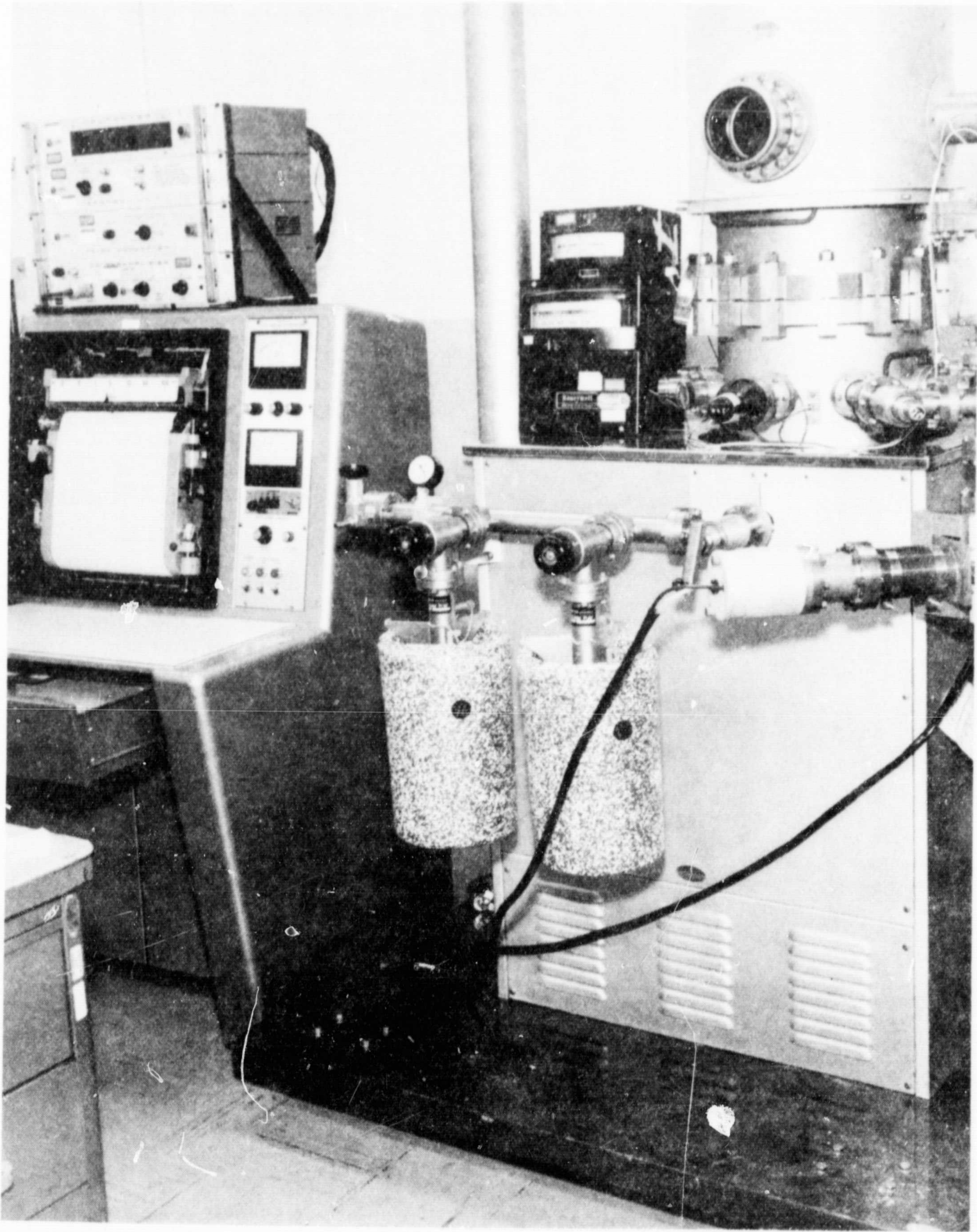
EXPLODED VIEW OF ION GUN



ION GUN ASSEMBLAGE WITH ELECTRON BEAM HEATER



ULTRA HIGH VACUUM STATION AND CONTROL PANELS



ULTRA HIGH VACUUM STATION AND MASS SPECTROMETER

R-25,488
Neg. 8704-8

Figure 11

has been constructed. With the ion beams directed in the vertical direction and the table moving perpendicular to the ion beam, a line is scribed on a glass substrate. Knowing the angle of the wedge and its position relative to the ion gun, the focal point (minimum beam diameter) as well as the beam spread can be measured.

Element Investigation

A number of single crystal electroluminescent (EL) elements were fabricated for comparison purposes in the survey of materials suitable for implementing a matrix display. Both silicon carbide (SiC) and zinc telluride-zinc selenide (ZnTe-ZnSe) junction devices were prepared. After junction formation, each element was metal electroded to provide current injection contacts. A subsequent acid etch of the top electrode was necessary to provide sufficient transparency for visible emission penetration.

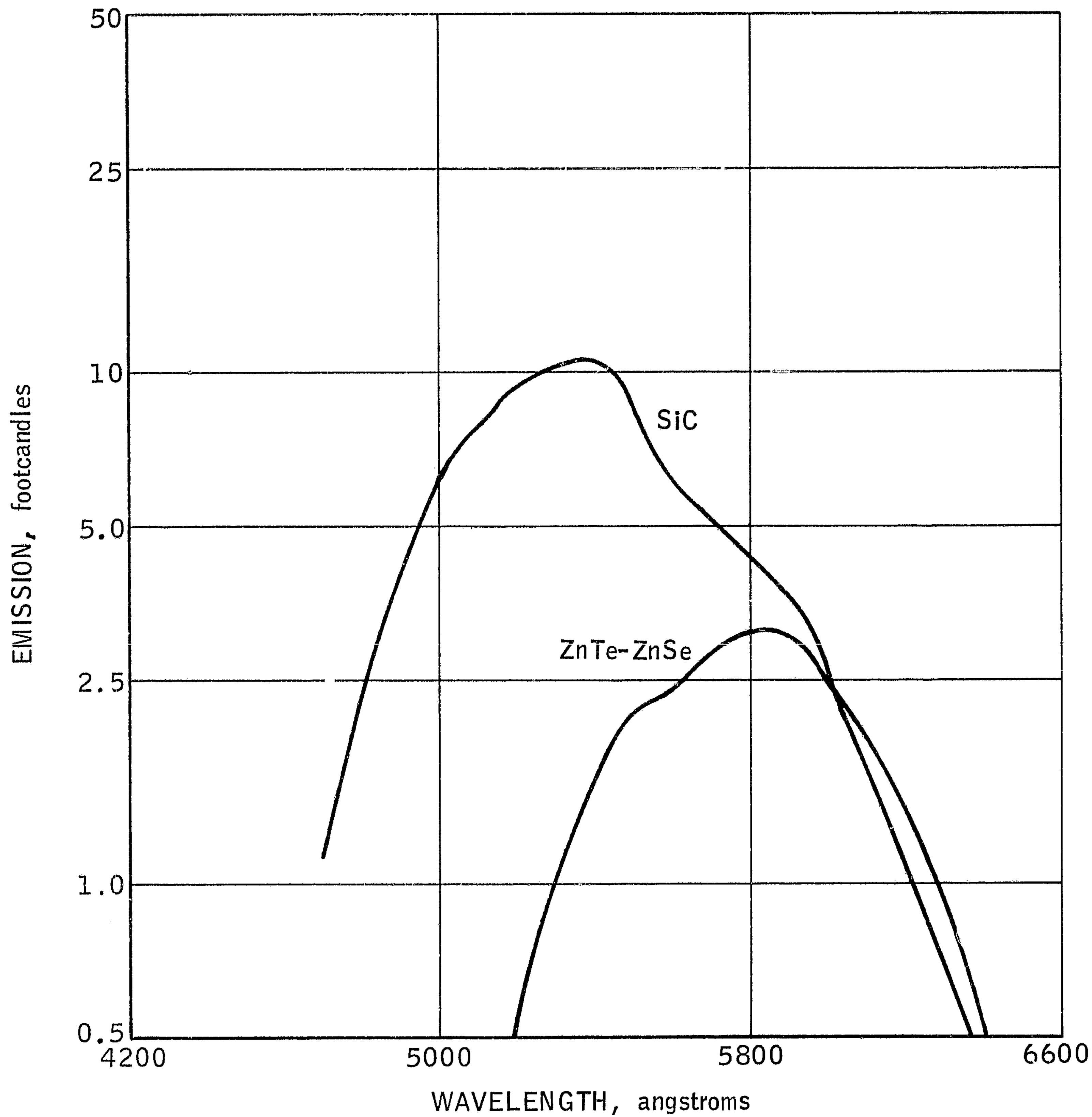
The light output from the EL cells was measured with a Gamma spectrophotometer which employs a photocell, a neutral filter, and a spectral filter with a band pass of 20 millicrons. The filter and photocell are calibrated against a standard lambertian white source. A fiber optic is used to capture the light emitted and to direct it to the photocell. Performance data for a SiC and a ZnTe-ZnSe cell is shown in Figures 10 and 11. Efficiency of the two cells was calculated to be respectively; 1.8% for the ZnTe-ZnSe cell and 2.5% for the SiC cell. In thin film form, however, it is anticipated that the ZnTe-ZnSe will exhibit a much higher efficiency. For the measurement, the spectrophotometer was centered at 5500 Å with a bandpass of 200 Å. This wavelength matches the peak sensitivity of the human eye. Figure 12 represents the light output as a function of the forward current. As indicated, the current requirements are in the low milliampere range. Figure 10 represents the spectral emission at constant current. (The operating points being respectively: SiC - 6 volts, 17.5 milliamperes and ZnTe-ZnSe - 6.5 volts, 8.3 milliamperes.)

Demonstration Model

To demonstrate the feasibility of the matrix configuration for addressing and storage a small array of discrete elements (7 x 5 elements) was constructed. This array consisted of carrier injection EL devices for light emission and avalanche diodes for storage of display data. The EL devices and diodes are arranged in matrix form by rows and columns with momentary contact switches for addressing purposes.

In essence, at each matrix point is a series combination of an EL diode, an avalanche diode, and a small resistor. The typical current-voltage characteristics of these components are shown in Figure 15. The composite characteristic is indicated by a heavy line. For sustained operation and triggering, this summation of the individual voltage drops provides knowledge of the required voltage. The matrix configuration is shown in Figure 16.

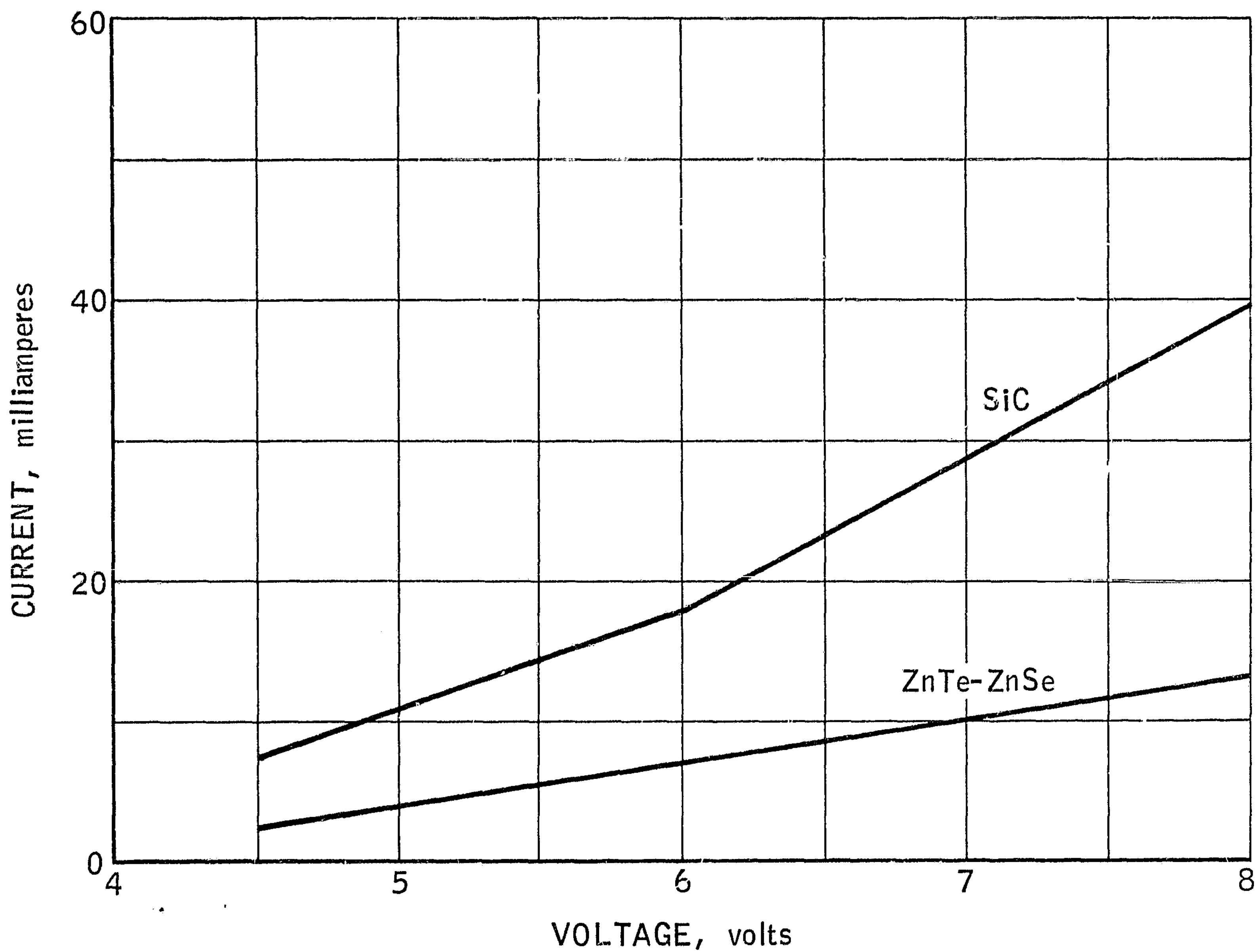
The EL units are conventional Silicon Carbide carrier injection diodes which provide a peak spectral emission at 5900 angstroms. A visible light output of 0.8 footlamberts per milliampere is available.



SPECTRAL RESPONSE OF EL CELLS

R-25,290

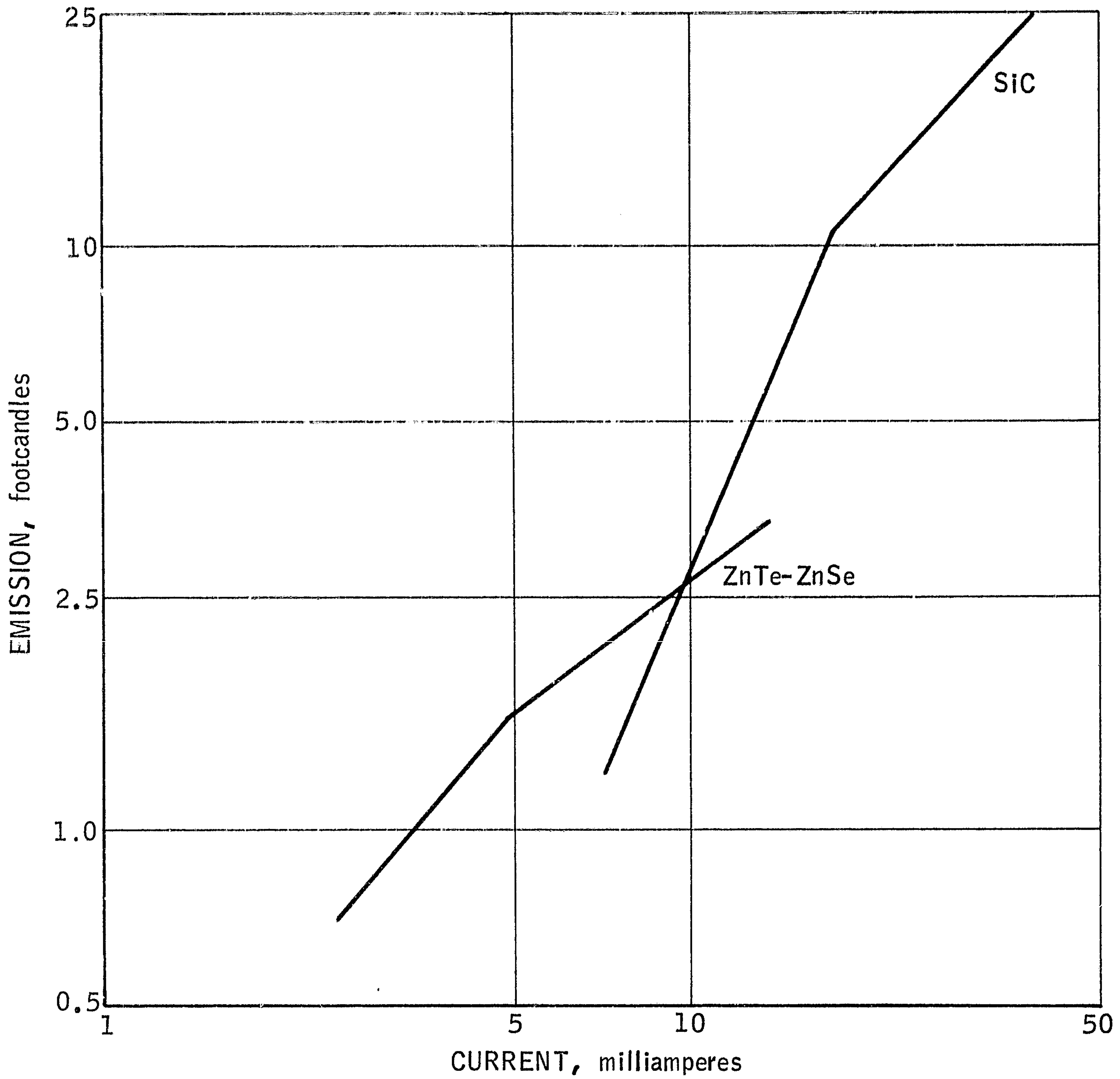
Figure 12



CURRENT-VOLTAGE CHARACTERISTICS
FOR EL CELLS

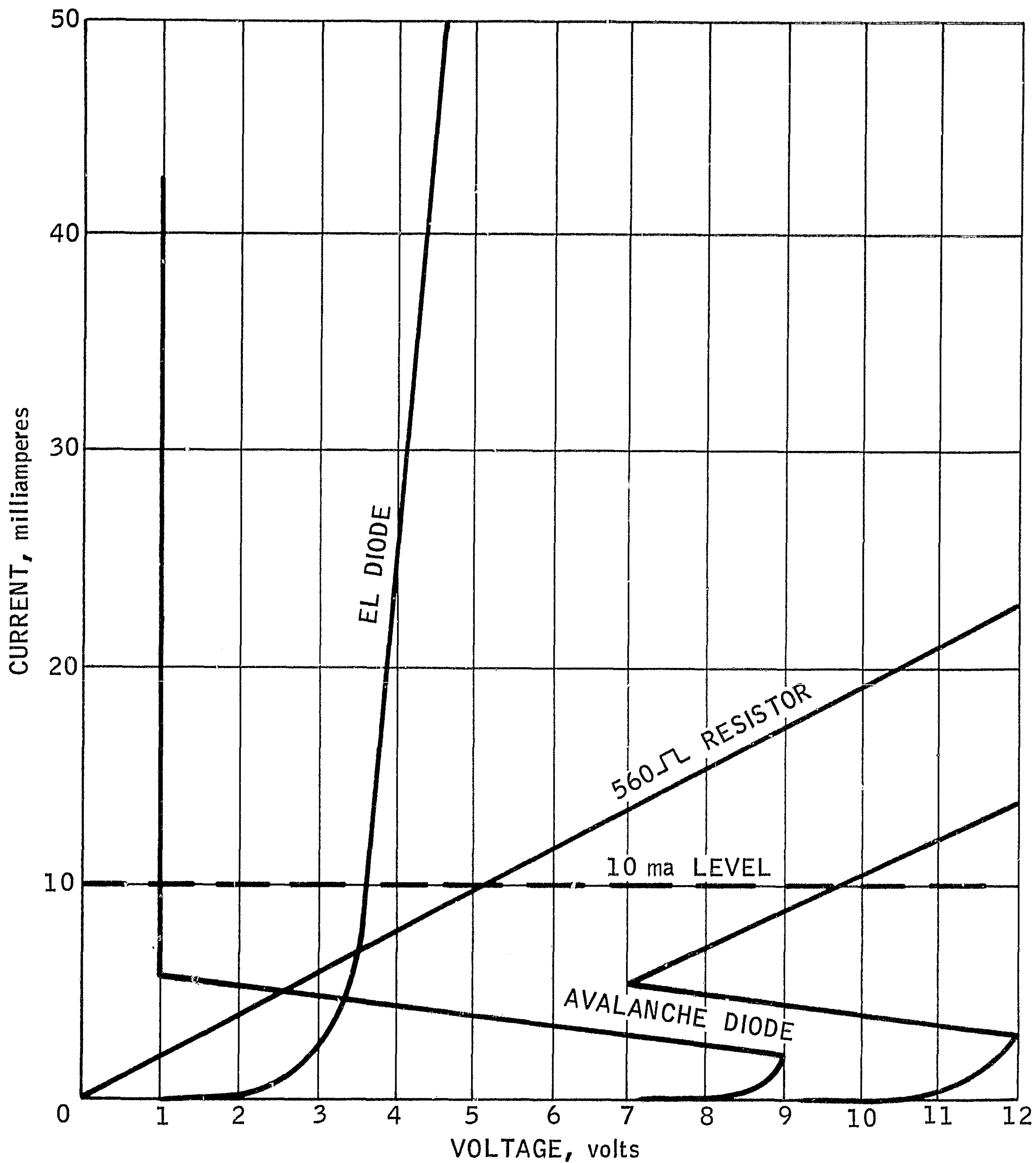
R-25,291

Figure 13



EMISSION-CURRENT CHARACTERISTICS

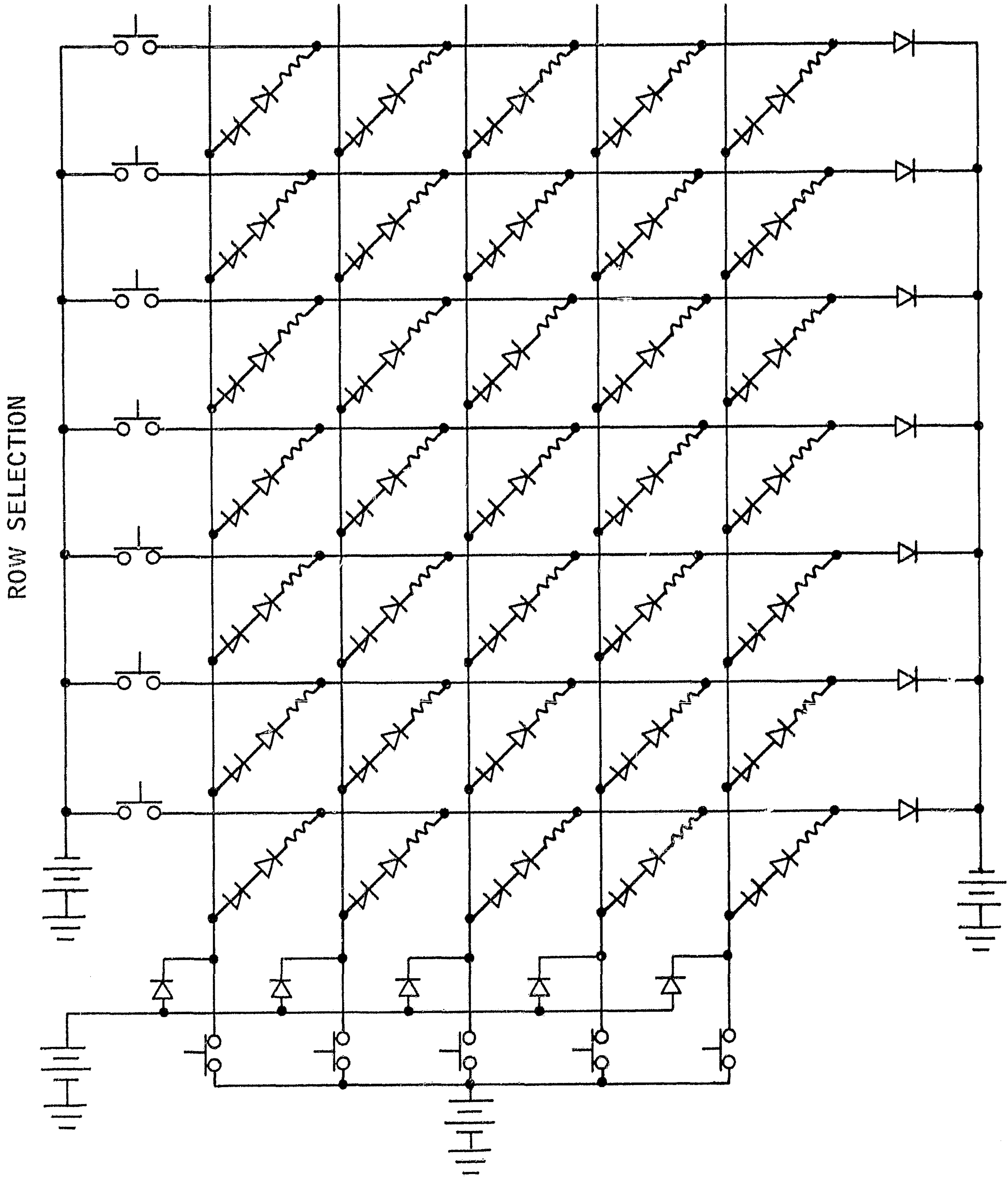
Figure 14



MATRIX COMPONENT CURRENT-VOLTAGE CHARACTERISTICS

R-25,486

Figure 15



R-25,485 MATRIX CIRCUIT CONFIGURATION Figure 16

The avalanche diodes are conventional four layer diodes with a low "break over" voltage of approximately 8 volts. The "forward on" voltage is nominally 1 volt.

Table III lists the various voltages necessary to address each matrix point. These voltages were obtained by measuring the voltage and current of the avalanche diodes necessary to cause avalanche at each matrix position. At this current level, the voltage drop across the associated EL diode was measured. An attempt was made to match avalanche and EL diodes to offset the wide range of tolerance of these devices. The holding voltages were obtained in the same manner.

TABLE III

Matrix Triggering Voltages

Matrix Position*	Avalanche Trigger Voltage	EL Diode Trigger Voltage	Total Trigger Voltage
1-1	17.1	0.15	17.25
1-2	16.3	1.1	17.4
1-3	18.0	0.05	18.05
1-4	16.5	1.08	17.58
1-5	17.4	0.4	17.8
1-6	17.3	1.25	18.55
1-7	16.8	0.84	17.64
2-1	18.0	0.08	18.08
2-2	17.3	1.55	18.85
2-3	17.8	0.08	17.88
2-4	17.5	1.09	18.59
2-5	15.5	1.05	16.55
2-6	16.9	0.43	17.33
2-7	17.0	1.09	18.09
3-1	17.5	0.52	18.02
3-2	17.7	0.1	17.8
3-3	17.0	0.43	17.43
3-4	16.9	0.12	17.02
3-5	17.5	0.54	18.04
3-6	17.2	0.3	17.5
3-7	16.3	1.29	17.59
4-1	18.0	0.6	18.6
4-2	17.7	0.25	17.95
4-3	16.7	0.56	17.26
4-4	16.9	0.26	17.16
4-5	17.3	0.1	17.4
4-6	16.9	0.49	17.39
4-7	16.8	0.42	17.22
5-1	16.8	0.72	17.52
5-2	17.5	0.06	17.56
5-3	17.8	0.39	18.19
5-4	17.7	0.46	18.16
5-5	17.4	0.1	17.5
5-6	17.3	0.4	17.7
5-7	17.4	0.15	17.55

* Matrix Position 1-1 indicates Column 1 and Row 1

CONCLUSIONS AND RECOMMENDATIONS

1. The II-VI compounds, and in particular ZnTe-ZnSe, appear most promising for the thin film implementation of low voltage carrier injection display panels on the basis of spectral response matching the human eye, direct electron energy level transitions, and an economical fabrication process.

2. Thin films of ZnTe appear feasible due to a new method of coevaporation which can provide the minimization of vacancy formation during deposition.

3. II-VI compounds, such as ZnTe, with low voltage excitation, have the capability for high level emission as confirmed by demonstration with discrete elements.

4. The proposed matrix configuration with storage appears feasible due to experimental results obtained from a demonstration model.

The development of low voltage electroluminescent devices with storage capability should continue and emphasize as the next step the development of the thin film technology required for economical fabrication.

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APPENDIX A

NEW TECHNOLOGY APPENDIX

NEW TECHNOLOGY

A new type of evaporating heater source was designed to permit the simultaneous evaporation of the elements of zinc telluride, ZnTe. Pages 4 to 8 describe this source.

APPENDIX B

STORAGE PRINCIPLE

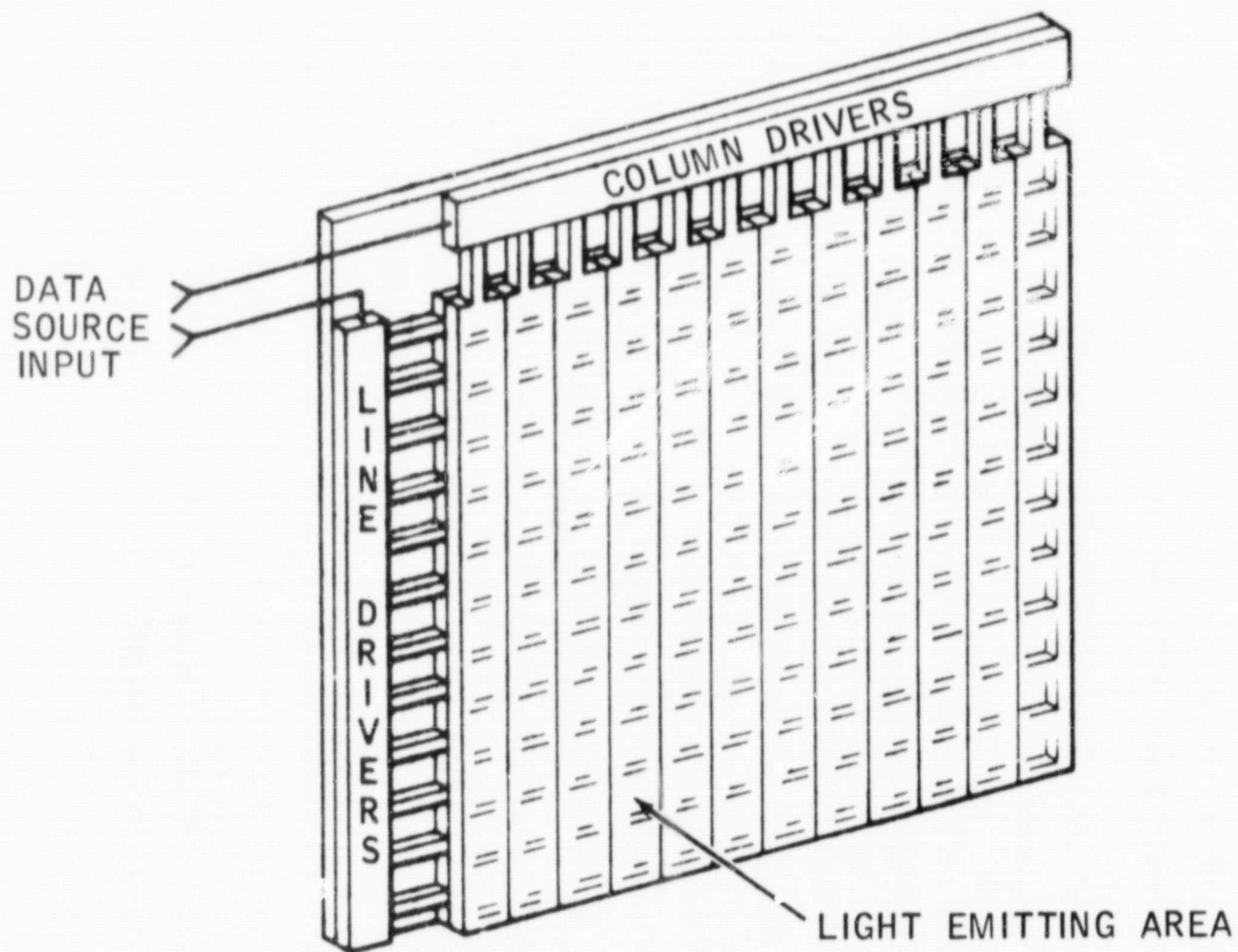
STORAGE PRINCIPLE

Marquardt's display panel (Figure 1) is composed of a thin film laminate of carrier injection EL (ELD) and avalanche injection diode (NRD) materials placed between electrodes and supporting substrates. A line grid of electrodes is deposited on each side of the laminate, the front electrode being transparent to allow the light to be emitted. By placing the grids at right angles to each other, the panel is effectively divided into small elements that can be addressed individually.

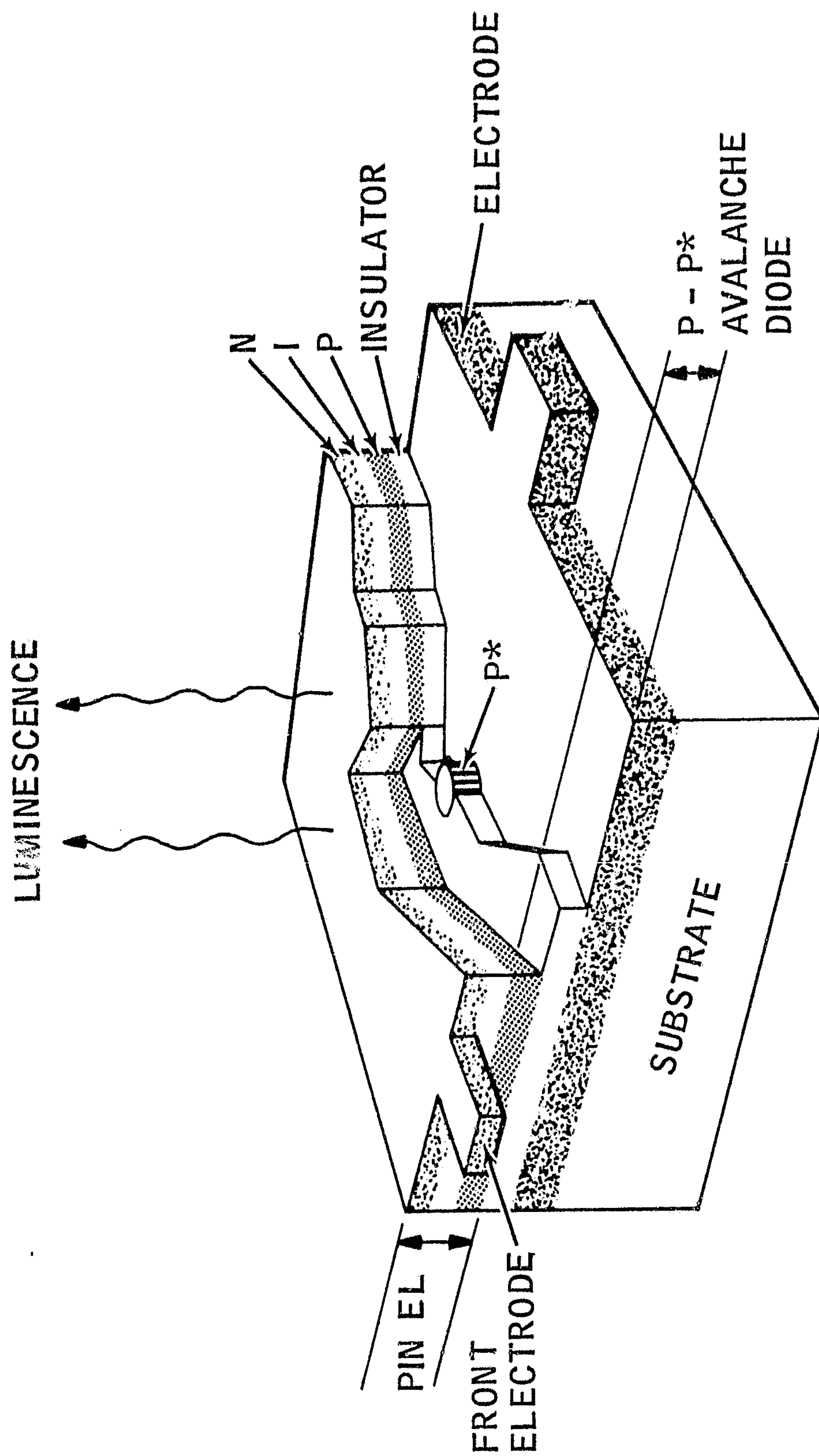
Basic Element

An elemental area of the laminate is shown in Figure 2. The light emitting mechanism of the laminate is composed of an insulating layer of EL-material which is intrinsic in nature between an electron injecting contact layer and a hole injecting contact layer. Ideally, the radiative emission will occur throughout the volume of the insulating layer. This device has a voltage/light relationship which is highly non-linear (see Figure 3a). Thus, no light is emitted at the junction of the EL-material until the voltage reaches a threshold value, V_o. Increasing the voltage beyond this value, leads into a nearly linear region where the light output is approximately proportional to the current and increases nearly linearly with the applied voltage. (If employed in a matrix display panel, the highly nonlinear characteristic of the carrier injection EL-material alone would provide an efficient means for suppressing unwanted luminescence in adjacent elements; however, each element will luminesce only as long as the voltage is applied to the matrix lines).

The holding or memory mechanism of the laminate is provided by a highly negative resistance phenomena resulting from electron collision avalanche in the diode (NRD) material. This effect can be obtained by proper doping of a host crystal such as zinc telluride or other materials such as silicon or germanium. The current to voltage relationship of this type of avalanche diode is characterized by an ohmic region (very low conduction), an avalanche region where the resistance is sharply negative and a current multiplication region (very high conduction), see Figure 3b. The transition from the ohmic region into the avalanche region occurs in nanoseconds at the trigger or turnover voltage, V_M.

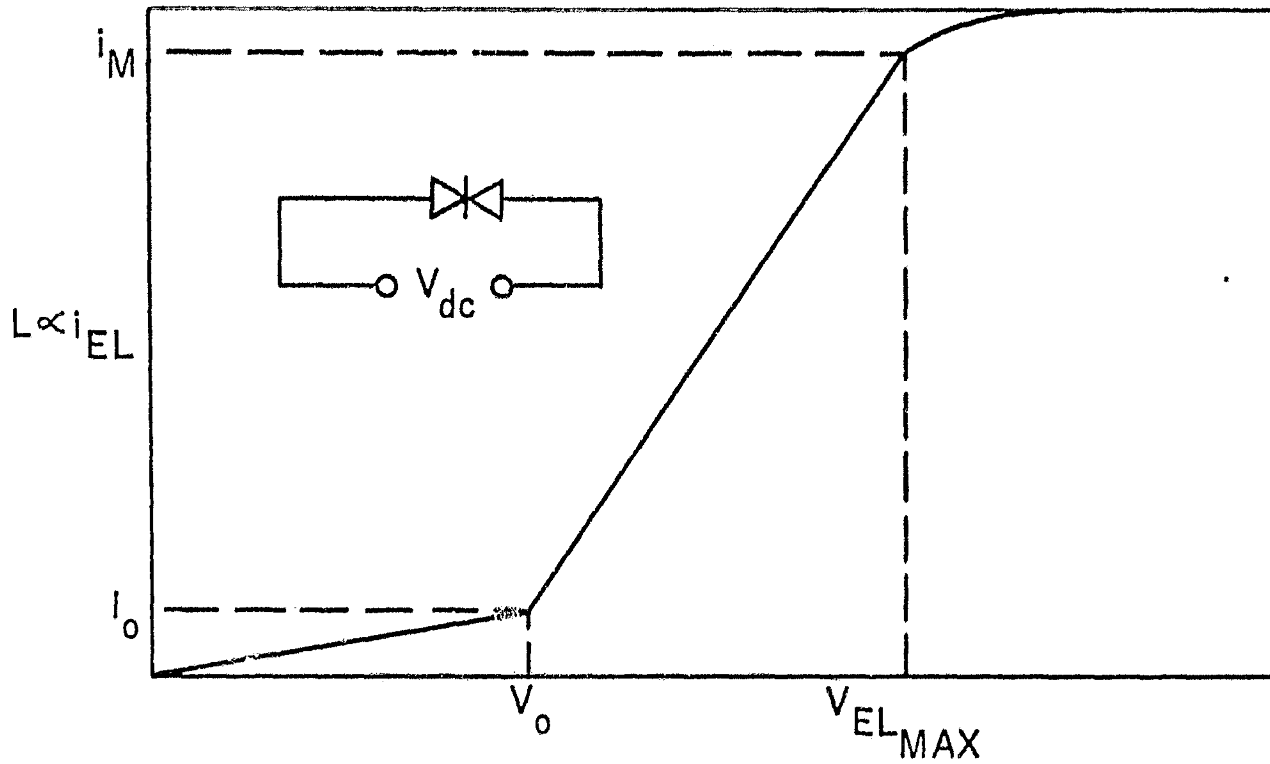


ELECTROLUMINESCENT MATRIX DISPLAY PANEL

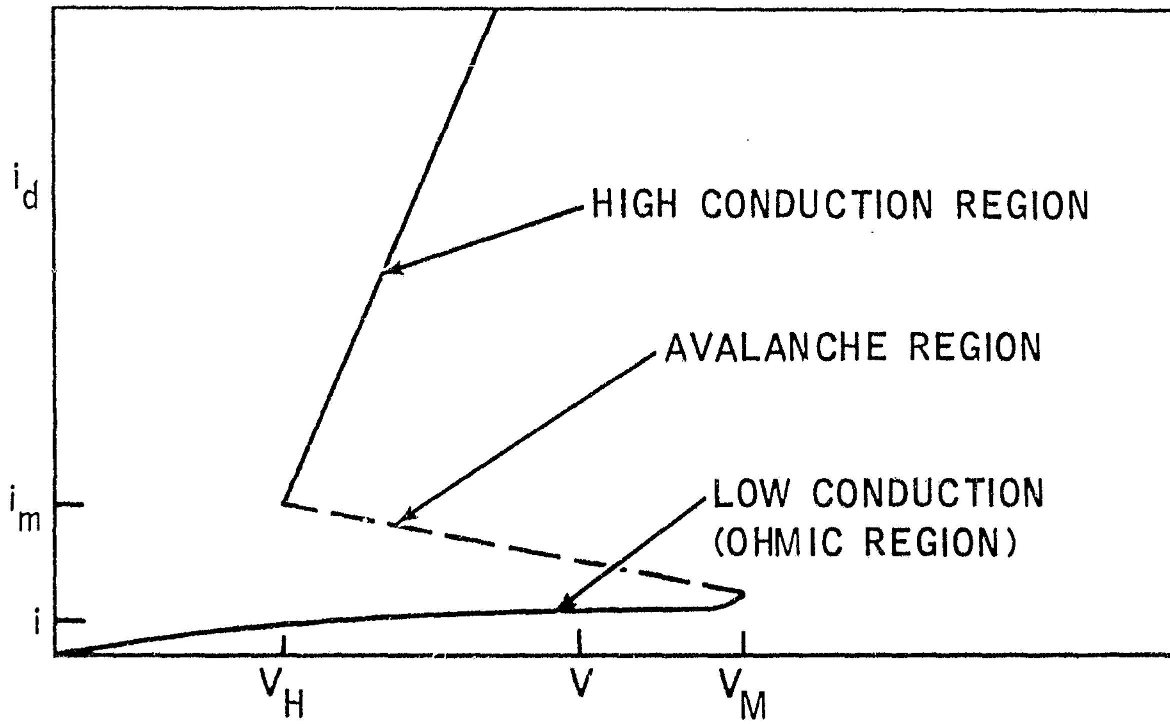


DISPLAY ELEMENT

Figure B-2



(A) INJECTION EL VOLTAGE VS LIGHT (L) OUTPUT
(PARTIAL CHARACTERISTIC)



(B) AVALANCHE INJECTION DIODE CHARACTERISTIC

CHARACTERISTIC CURVES

Figure B-3

When the applied voltage exceeds V_M, the avalanche mechanism takes over and the current delivered abruptly increases. Once the avalanche condition has developed, the voltage (V_H) across the diode necessary to sustain the higher currents is considerably reduced. V_H is a characteristic of the bulk material. For example, the approximate V_H for germanium is 8V; silicon, 12V; and zinc telluride 15V.

The diagram shown in Figure 4 corresponds to the basic element discussed and comprises the negative resistance diode (NRD) which, for convenience, is shown distinct from the electroluminescent diode (ELD); the DC voltage source, V, and a load resistance R_L. The magnitude of the voltage, V, is selected according to the desired light output, and in the case of maximum light output from ELD, would assume a value:

$$V = V_{EL_{(max)}} + V_H + iR_L$$

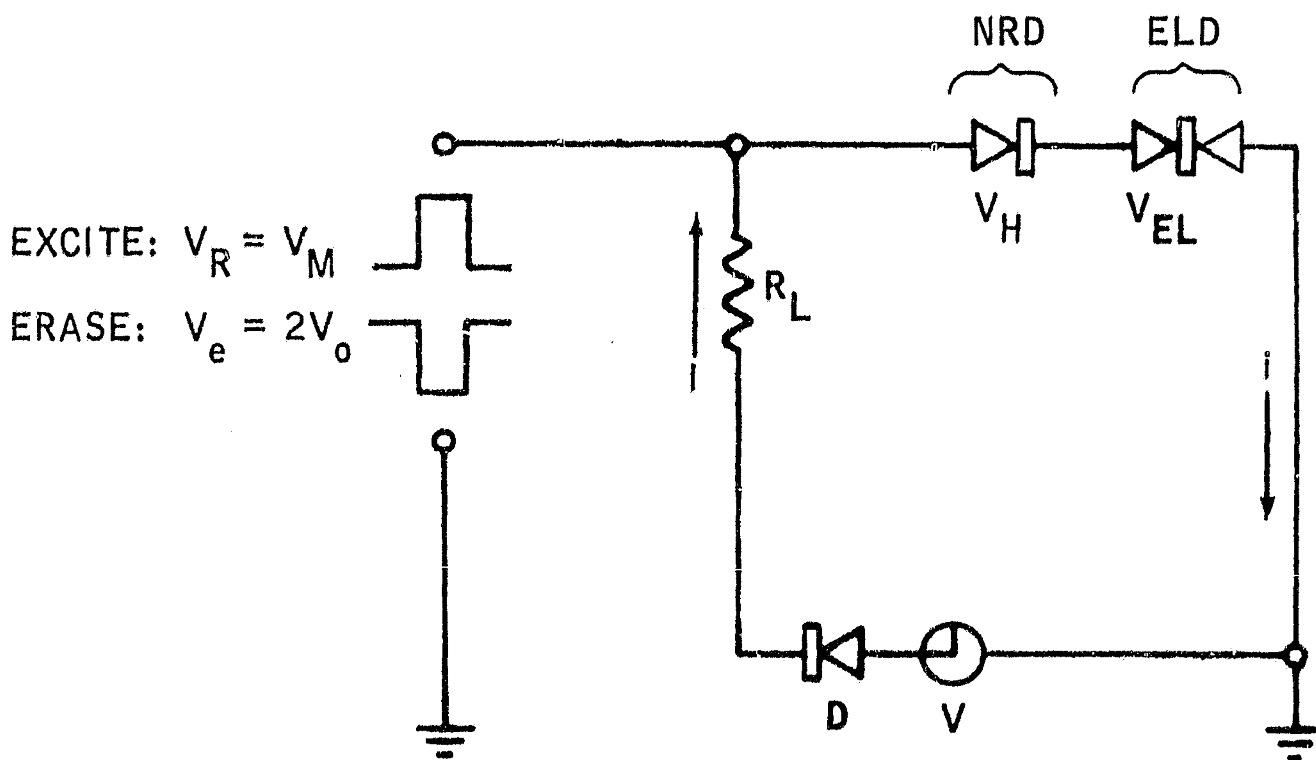
In such conditions, $V < V_M$ as shown in Figure 3b and the current, i, flowing through the loop is several orders of magnitude smaller than i_M which corresponds to the maximum illumination as shown in Figure 3a. Thus

$$V_H < V < V_M$$

although V is greater than V_{EL}, the loop resistance prior to triggering is extremely high due to the quiescent state of NRD, thus no appreciable current flows and no illumination arises from ELD. This quiescent state remains undisturbed until the NRD is triggered into avalanche.

READIN CONDITION: To allow a sufficient current to flow in the loop to permit the ELD to luminescence, avalanche must be started in NRD. To do so, either V must be increased and made at least equal to V_M or an external voltage must be applied in the form of a readin pulse, V_R, which must supply the same peak voltage as shown in Figure 4.

To prevent the readin pulse from dissipating uselessly in load, R_L, when triggering the avalanche diode, a second diode, D, may be substituted for R_L or added in series. In the strict point of view of operation, R_L and D play the same role, i.e., an impedance to couple the source, V_R, to the loop. Since the diode is back biased during triggering, its impedance is very high (its breakdown voltage being greater than V_R). Thus, the diode D does not draw power from the trigger source. Conversely, with regard to the source, V, for which the diode is forward biased in the absence of V_R it presents a negligible dissipating impedance in the loop.



EQUIVALENT CIRCUIT

When avalanche occurs by the application of V_R, the potential across the elements of the loop reaches a new equilibrium with a drop equal to V_H across NRD and V_{EL} across ELD and the current in the loop assumes a value i_m: where $i_o < i_m \leq i_M$ as shown in Figure 3a and 3b. This condition is sufficient to sustain the avalanche mechanism and to provide a constant current flow. Removal of the trigger pulse, V_R, does not affect the operation after avalanche has started. The time necessary to secure avalanche and switch from the quiescent state to a stable negative resistance operation does not exceed 10 nanoseconds.

The point, V_H, is a stable and highly reproducible characteristic for a given device built into a given material, thereby the combination NRD-ELD is also stable and ELD will luminesce proportionally to the amplitude, V_{EL}, appearing across this diode.

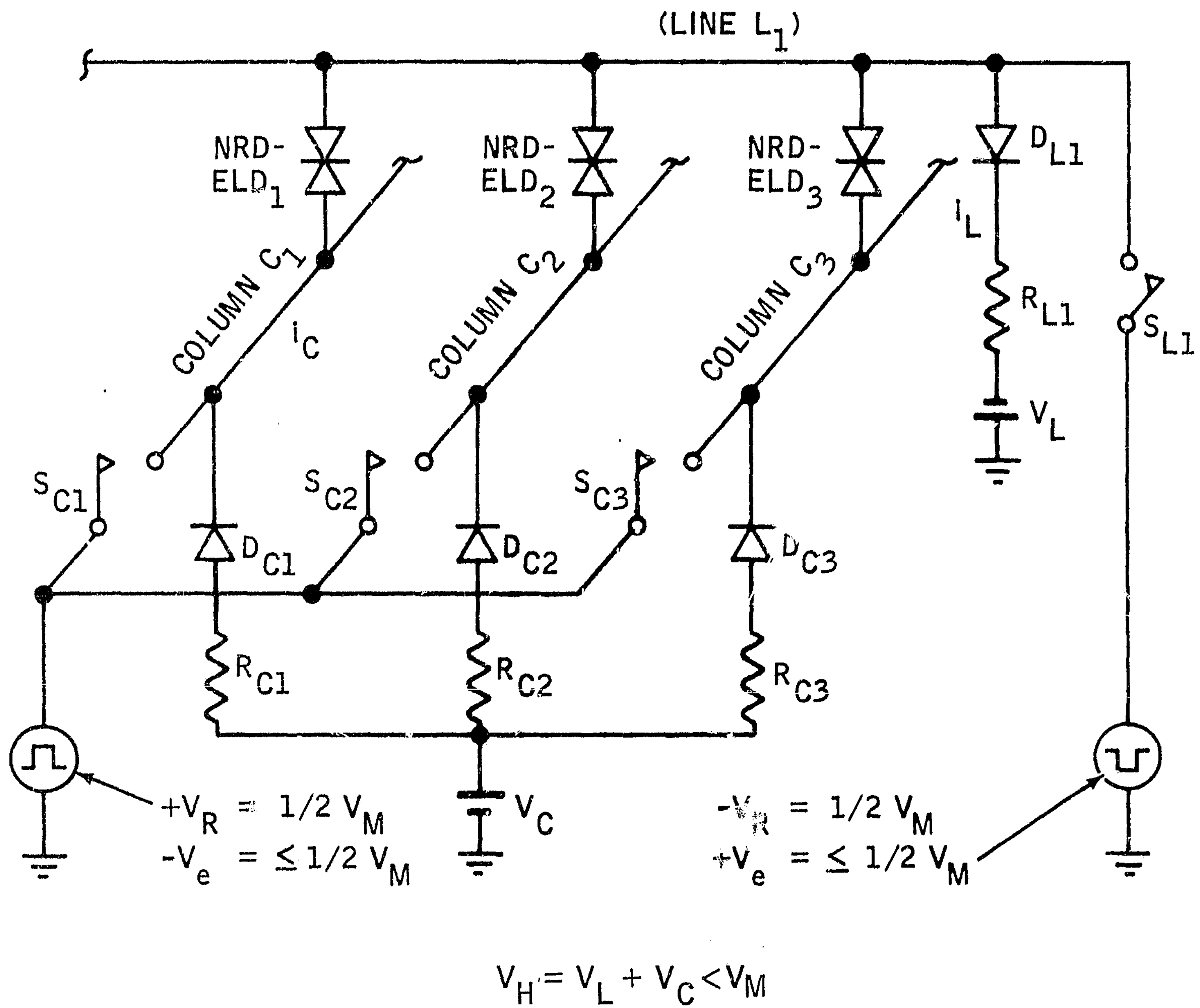
$$V > V_{EL} \geq V_{EL_{max}}$$

Therefore, electroluminescence will hold on as long as V is applied to the circuit.

ERASE CONDITION: The EL-excitation is stopped by interrupting the avalanche condition of the diode. This condition can be accomplished by the application of a pulse of opposite polarity, as shown in Figure 4, that would effectively remove the bias voltage, by current reversal in the load R_L, or by decreasing the current in the loop below the point, i_m, of the NRD, as shown in Figure 3b. The amplitude of the erasing pulse need not be greater than $V_e = V - V_H$, since the objective is to decrease the current in the loop to $i_e < i_m$. The duration of the erase pulse, V_e, is a function of the closed loop transient conditions and at most would be 40 nanoseconds.

2. EL Matrix Operation

In Figure 5 three of the above described elements are illustrated in a matrix configuration connected to one line and three columns and their respective ohmic load resistors (R_L) and DC sources (V_L and V_C). For addressing a specific intersection to be triggered on, i.e., the EL-element to be illuminated, a positive pulse ($+V_R$) of 1/2 V_M amplitude on the selected column and a negative pulse ($-V_R$) of 1/2 V_M amplitude on the selected line are simultaneously applied. This effectively applies a total voltage across the addressed NRD-ELD that is sufficient to



$$V_H = V_L + V_C < V_M$$

THREE ELEMENT MATRIX OPERATION
(SIMPLIFIED SCHEMATIC)

Figure B-5

switch the NRD diode into an avalanche condition, i.e., $V_M = 2V_R$. During the pulse ($\pm V_R$) period, the voltage across the selected cell settles to the sustaining value (V_s) as determined by the DC sources,

$$V_s = (V_L + V_C) - i \cdot 2R_L = V_H + V_{EL}$$

Typical values might be $\pm$ 15 volts for V_L and V_C, 10 milliamperes for i_m and 500 ohms for R_L to obtain a sustaining voltage of 20 volts across both the EL and avalanche diode. The avalanche diode of silicon used in the experiment had a characteristic voltage (V_H) of 12 volts providing 8 volts for the injection EL-element which delivered a brightness in excess of 30 foot-lamberts in the zinc telluride junction.

Adjacent elements on the selected line or column are prevented from being triggered from the interrogation pulses by receiving inadequate voltage levels to start the avalanche mechanism. This can be seen from Figure 5, where the applied voltage across an unselected cell amounts to at most V_R plus either V_L or V_C. As previously stated, V_L and V_C are selected such that their sum is equal to $V_H + V_{EL} + i \cdot 2R_L$ but less than V_M. Therefore, the transient read voltage appearing across any of the unselected elements is at most equal to $V_R + V_C$ V_M, preventing these NRD elements from being excited into avalanche and the EL cannot luminesce.

The process of erasing an energized element is accomplished by applying voltage pulses of the opposite polarity to the line and column sufficient to momentarily stop the current flow in that element, or, as seen before, at least reduce the current below i_m. Assuming, for example, that all the elements, ELD_1, ELD_2, ELD_3 have been energized and only one point is to be erased selectively, such as ELD_1, at the intersection of line L_1 and Column C_1. A negative voltage pulse ($-V_e$) will be applied to column C_1, simultaneously with a positive pulse ($+V_e$) to the line as shown in Figure 5. These pulses although having no direct effect on the NRD-ELD element to be erased, back bias that element with regard to the other elements of the circuit. The pulse ($-V_e$) drives the diode, D_{C1}, in the forward direction and the resulting added current flow in R_{C1} reduces the total voltage applied to ELD_1 from the source, V_C. Similarly, the pulse ($+V_e$) applied to the line, L_1, produces the same effect on D_{L1}, and its load, R_{L1}, thereby reducing further the voltage applied to ELD from the source, V_L.

In effect, the sum of the $-V_e$ and $+ V_e$ erase pulses will reduce the total voltage applied to ELD_1 sufficiently to bring the current in that loop below its i_m point and, therefore, will stop avalanche in that element. All the other points, ELD_2, ELD_3, will be decreased only

by a fraction of the sustaining voltage (approximately equal to V_e only) which is not sufficient to lower the current in these elements to their i_m point. Therefore, those points which receive only half the erase signals will be decreased slightly in luminous intensity only for the duration of the erase period. Since, as previously stated, the time required to turn off avalanche in the NRD is only 30 to 40 nanoseconds, the decrease in light intensity during this short interval is not normally perceptible. As soon as the erase pulse is removed, these half selected elements return to their normal emission level and the storage function is maintained.

4. Other Features

The use of color in displays provides an additional dimension in conveying intelligence. Similarly, the use of a gray scale adds depth to a pictorial display. The proposed carrier injection concept permits implementation of both features. Possible configurations are discussed in Appendix B.