

Materials Aspects of Display Devices

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With the rapid growth in versatility and complexity of electronic systems, display devices are becoming an increasingly crucial element in the efficient transfer of information from these systems to the human operator. Because of the variety of demands placed on displays to satisfy existing and future requirements in industrial, consumer, and

as the ubiquitous device for displaying electrical information in computer terminals and word-processing and related information systems.

Although the cathode-ray tube is still dominant in these areas, intense effort is now under way to develop new display technologies and associated materials. This interest can be traced to the grow-

Summary. For many years interest in display devices stemmed almost entirely from the needs of television receivers, oscilloscopes, and radar systems whose requirements were almost ideally satisfied by the cathode-ray tube. However, during the past two decades the proliferation of small electronic instruments with digital output has stimulated the development of a number of new display media which, because of their compact nature and low power consumption, are better suited for such applications. In view of the success achieved with these technologies a continuing effort is being directed toward increasing their information capacity to the point where they may ultimately be useful in applications now requiring cathode-ray tubes.

military applications, the field of display technology is today in a state of considerably flux, with numerous devices, both old and new, competing with each other to capture portions of a large and rapidly growing market.

For many years the dominant display medium has been the cathode-ray tube. In 1897 (some months before the publication of J. J. Thomson that established with certainty that "cathode-rays" consisted of electrons) the cathode-ray tube was invented by F. Braun as an instrument for the visualization of rapid time-varying electrical signals. Since then the successive improvements made in it have resulted in today's highly sophisticated oscilloscopes. By about 1930 it became clear that the cathode-ray tube was almost ideally suited for producing television images, resulting in the virtual cessation of work on all other display technologies. During World War II, the cathode-ray tube found an important new role as the display medium in radar systems, whose development could hardly have been possible without such tubes. In more recent years the cathode-ray tube has emerged in still another role

ing need during the 1950's for small devices capable of displaying numerical information in applications such as high-speed pulse-counting. This need was satisfied by the Nixie gas-discharge tube which could display any one of ten digits in a fixed format. With the subsequent growth of semiconductor and digital technology a great variety of small, low-power instruments emerged for which it was desirable to have even more compact numeric or character displays capable of operating at lower voltage and with reduced power consumption—application areas for which the conventional bulky, high-voltage cathode-ray tube was hardly appropriate. These instrument requirements stimulated work on other technologies, particularly light-emitting diodes and liquid crystals as well as improved types of gas-discharge devices.

The success achieved in producing simple displays with these new technologies soon stimulated efforts to develop devices with larger capacity, capable, for example, of displaying tens or hundreds of numerals or characters. As commercial devices emerged containing

an increasing number of display elements, the realization arose that these technologies might be even further extended to satisfy application areas previously considered only the province of the cathode-ray tube. Although the development of display devices capable of competing with the cathode-ray tube (that is, having comparable numbers of picture elements, speed, gray scale, and color) remains a formidable task, major development programs are now under way with this objective. Motivation for this research is in no small measure attributable to the increasing saturation of the television market in many countries and the resultant intense rivalry between companies to produce new television displays in panel form without the size limitations of the cathode-ray tube.

As in the case of other areas of electronics, display systems have profited greatly from the development of semiconductor technology, especially where local information storage and complex addressing schemes are involved. However, the advances in semiconductor technology, characterized by the ever-increasing number of low-power circuit elements which can be packed onto a small semiconductor chip, have been of little direct aid in the development of most display devices. For display purposes optically active materials extending over large areas are required (difficult to achieve with semiconductor crystals of limited size), and the sequential switching of substantial power to a very large number of elements is frequently involved.

The different display technologies now under investigation make use of a bewildering array of physical and chemical phenomena, encompassing materials in the solid, liquid, and gaseous states. In the sections that follow, however, the discussion will be focused primarily on the major technologies and associated materials, particularly those which have attained some degree of commercial acceptance.

Cathode-Ray Tubes

Since their inception, cathode-ray tubes have depended on luminescent screens of powder material (referred to as "phosphors") to convert the energy of the scanning electron beam to light. Although naturally occurring minerals were used in early tubes, these materials have long since been supplanted by syn-

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thetic phosphors with far superior characteristics. Because of the requirements of high stability under electron bombardment, low vapor pressure, and the ability to withstand tube bakeout temperatures in excess of 400°C, only selected inorganic compounds have been found useful. Among these are the sulfides, selenides, silicates, tungstates, and oxides of zinc, cadmium, calcium, and magnesium (1).

All phosphor powders consist of crystalline particles and generally depend for their luminescence on the incorporation of a small amount of one or more "activators" (usually metallic elements such as copper, silver, manganese, chromium, and bismuth). By controlling the quantity and type of activator (as well as the procedures) used during synthesis the characteristics of the phosphor (for example, efficiency, color of luminescence, and decay time) can be varied (1, 2). Associated with the activator atoms or ions incorporated in the host crystal are a number of discrete energy levels, the lower ones being normally occupied. During bombardment by the high-energy electron beam, the luminescent centers corresponding to the activator atoms are excited, producing light as they relax to their lower energy state. All present phosphors are wide-band-gap (> 3 electron volts) materials, making them transparent to the light internally generated. With few exceptions the materials are highly insulating, any conductivity which does exist generally resulting from electron, rather than hole, mobility.

Of the more than 50 different commercial phosphors available, perhaps a third are group II-VI compounds such as ZnS, (Zn,Cd)S, and Zn(S,Se). These are used in a variety of applications and are of particular importance in color television tubes where, for example, ZnS:Mg (that is, ZnS activated with Mg) is used to produce blue emission and (Zn,Cd)S:Cu,Al is used to produce green emission. Phosphors of these types are characterized by high efficiency, materials such as ZnS:Ag and ZnS:Cu being capable of converting more than 20 percent of the electron-beam energy to light. Such high efficiencies allow brightness levels of more than 100 foot-lamberts (fL) to be readily obtained in commercial television receivers.

Another important phosphor used in many applications is $\text{Zn}_2\text{SiO}_4\text{:Mn}$ whose luminescence is green. Although its efficiency is less than half that of the II-VI phosphors it is extensively used in applications where its ability to withstand intense electron bombardment for long periods with minimal degradation is impor-

tant. Typical of such applications are oscilloscopes, projection systems, and cockpit displays where maximum brightness is required.

The most recently developed types of phosphors are those containing rare-earth activators (3), particularly terbium and europium. The stimulus for the development of these phosphors arose from the need in color tubes for a red-emitting phosphor whose efficiency was comparable to the green and blue phosphors. The first rare-earth phosphor to be developed was $\text{YVO}_4\text{:Eu}$, which was introduced in 1964. This has been superseded by the more efficient $\text{Y}_2\text{O}_3\text{:Eu}$. It is of interest that because of the high efficiency obtained with red phosphors research is now being redirected toward improvement of the green phosphors. For other applications several additional rare-earth phosphors have been developed (4) such as green-emitting $\text{La}_2\text{O}_3\text{:Tb}$ and white-emitting $\text{Y}_2\text{O}_3\text{:Tb}$.

Aside from their long operating life, rare-earth phosphors are important because of their relative freedom from saturation at high input power levels. Unlike the broad emission spectrum of other phosphors, the emission from rare-earth phosphors is confined to one or more very narrow bands (less than 1 nanometer at half value). This allows the screen to be viewed through a narrow-band filter which blocks the reflection of external light at all other wavelengths, thereby enabling high-contrast images to be produced in high ambient light environments (such as airplane cockpits).

For applications such as television, phosphors are used whose persistence is less than the frame time of 30 to 40 milliseconds. For use in radar, where the time to scan a frame may be a second or longer, special phosphors have been developed such as (Zn,Cd)S:Cu whose yellow-orange persistence is of the order of seconds. Since the persistence of this material is maximized when it is optically excited (instead of electron-beam excited) it is coated with a layer of ZnS:Ag whose blue emission under electron bombardment causes luminescence in the (Zn,Cd)S. At the other extreme, phosphors with very short persistence have been developed for use in flying-spot scanners and photographic applications. A phosphor of this type is calcium-magnesium silicate activated with cerium (emitting in the violet and ultraviolet) which has a decay time of about 0.1 microsecond.

Typical phosphor screens consist of particles 1 to 10 micrometers in diameter deposited on the glass faceplate of the tube with a small amount of binder such

as potassium silicate. To absorb most of the energy of the penetrating electron beam, the layer is usually made several particles thick. However, because of light scattering, the resolution is limited to a few tens of micrometers. Although the resolution can be improved by using smaller particles, this usually results in lowered phosphor efficiency since the "dead layer" which covers the particles then absorbs a greater fraction of the electron-beam energy. For very high resolution, thin phosphor films produced by evaporation or vapor-phase reaction methods have been made with materials similar to those used for powder phosphors. Although their intrinsic luminescent efficiencies are comparable to powder materials, their effective efficiency is reduced to about 10 percent of this because of the high index of refraction of the film which prevents the escape of most of the light from the smooth surfaces.

Much of the present work on phosphors is concerned with the development of materials with special characteristics of color, persistence, and reduction of saturation at high brightness levels as well as increased efficiency and life. Despite the increased understanding of the luminescence of solids resulting from advances in solid-state physics, the complex physical processes occurring in the excitation of electron-bombarded phosphors (particularly powder materials) are in many respects understood only qualitatively. The development of new phosphors with specific characteristics, although guided by theoretical considerations, thus remains to a large extent dependent on experimental procedures.

Electroluminescent-Layer Displays

For many years the remarkably good performance obtained with phosphors excited by electron bombardment was a challenge to workers to develop similar screens that could be made to luminesce by direct application of a voltage across them. As far back as 1937, G. Destriau showed that light could be obtained from specially prepared ZnS powder layers when an a-c electric field was applied. Unfortunately, because of the unavailability at that time of satisfactory transparent electrodes for viewing the phosphor and the use of castor oil as a liquid dielectric to embed the particles, this work was either ignored or not considered seriously by the scientific community. In 1950, however, workers at Sylvania, using similar phosphor powder, were successful in fabricating more prac-

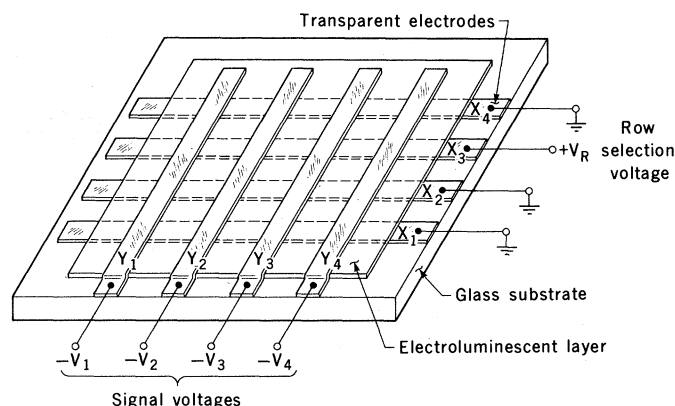
tical cells in which the powder was embedded in a solid dielectric and which employed recently developed transparent conductive coatings of tin oxide on glass. Since then considerable research effort has been directed toward improving electroluminescent phosphors and developing display devices based on these materials (5). Unlike the large number of materials which are relatively efficient under electron bombardment, in the case of electroluminescent layers acceptable efficiency has been obtained from few materials other than ZnS or closely related compounds such as Zn(S,Se).

In preparing ZnS powders for use in a-c-excited layers sufficient copper is added so that, in addition to its incorporation in the crystal as an activator, isolated regions of Cu_2S are formed on the surface or interior of the grains, resulting in the formation of Cu_2S -ZnS heterojunctions (6). When a-c voltage is applied across a powder-binder layer most of the voltage drop during a particular half-cycle appears across those junctions which are oriented in the back-biased (high-resistance) direction. Free electrons in these regions are then accelerated, causing ionization of luminescent centers by collision processes, with subsequent capture of the electrons in nearby traps. Upon reversal of the field these electrons are released, some of them recombining with the ionized centers to produce light. During alternate half-cycles similar action occurs at junctions oriented in the opposite direction so that a light pulse is produced each half-cycle.

Electroluminescent layers of the above type are usually about 25 to 50 μm thick, with the powder embedded in an epoxy or other organic binder. In typical operation an a-c voltage in the range of 100 to 200 volts root mean square (rms) is applied at some frequency in the range of 50 to 5000 hertz. At the higher frequency and voltage levels a steady-state brightness can be obtained which is adequate for viewing in moderate room light. Although considerable work has been done to develop practical display devices with such layers, the poor life often obtained (for example, more than 50 percent drop in efficiency after several hundred hours), their limited brightness under pulsed conditions, and the lack of a sharp threshold voltage for turn-on (important for addressing large arrays of elements as discussed below) has discouraged use of these materials.

About 10 years ago a new type of powder-binder electroluminescent layer was developed that can be excited with d-c (or pulsed d-c) voltage and whose char-

Fig. 1. Electroluminescent-layer display with X-Y addressing electrodes.



acteristics are considerably more desirable for display applications (7). As before, ZnS powder is used but with Mn as the activator. During preparation the powder particles are coated with a relatively heavy layer of conductive Cu_2S . When d-c voltage is initially applied across a layer of such particles held together with a limited amount of binder a relatively high current flows because of the particle-to-particle contacts, but no light is produced. If the d-c voltage is gradually increased (up to about 60 V, for example) during a period of about a minute a "forming" process occurs in a thin portion of the layer adjacent to the anode in which copper ions diffuse into the ZnS. This causes a marked increase in resistivity with most of the applied voltage drop now appearing across this portion of the layer. If d-c (or pulsed d-c) voltage of the same polarity whose magnitude is comparable to or higher than the voltage used in forming, is now applied, substantial yellow-orange light emission, characteristic of the Mn activator, is generated in the insulating region. Somewhat similar to the case of a-c powder material, light emission is attributed to excitation of the Mn luminescent centers (either directly or indirectly) by energetic electrons accelerated in the high-field region.

Because of the relatively high light output obtained with short d-c pulses and the sharp threshold voltage, such layers are of considerable interest for display devices containing a large number of picture elements. To reduce the number of electrical connections that would be required if each picture element of a large array had a separate lead, an X-Y addressing scheme is used such as shown in Fig. 1. As indicated, the electroluminescent layer is sandwiched between two sets of orthogonal conductors, the individual picture elements being defined by the crossover region of the electrodes. (To permit viewing of the light the X-electrodes on the glass sur-

face are made transparent.) In operation a pulse voltage, $+V_R$ is applied to one of the row conductors, for example, X_3 , and pulse voltages, $-V_1 \dots -V_4$, are simultaneously applied to the Y-conductors. This causes voltage pulses of varying magnitude above the threshold voltage, V_T , to appear across the elements of row X_3 , producing corresponding variations in light output. Negligible light output is produced, however, from the phosphor elements of all other rows since it is assumed that the voltages across them are all below the threshold voltage. By applying the pulse voltage, $+V_R$, to successive rows and cyclically repeating the addressing process at a rapid rate a flicker-free image can be produced. Experimental panels of this type have been developed for displaying both alphanumeric information and television images (8). For the latter purpose panels up to 20 by 27 centimeters in size have been built with 224×224 elements. By using pulses up to about 250 V across the phosphor elements images were obtained with good gray scale and a highlight brightness of 10 fL (about 1/10 of the 100-fL brightness obtainable with commercial television receivers).

As an alternative to powder layers, effort has also been directed toward the development of thin-film electroluminescent layers. Although initial attempts to produce such films resulted in poor light output and short life, significant improvements in such materials were made by workers at Sigmatron during the period of 1964 to 1970 using manganese-activated ZnS. These films (about 1 μm thick), requiring about 200 to 300 V of a-c for operation, were provided with an additional insulating film on one or both sides to prevent breakdown (5). By coating the rear surface of the phosphor with an additional light-absorbing layer of arsenic selenide the transparent phosphor was made to appear black in the off state (as opposed to the diffuse white appearance of powder layers). Information dis-

played with such films could thus be viewed with good contrast even in high ambient illumination.

Subsequent work by the Sharp Company with the same material (9) has resulted in thin-film phosphors capable of higher light output and extremely long life (in excess of 10,000 hours). The ZnS film, in this case 0.5 μm thick, is sandwiched between two thinner insulating films of Y_2O_3 . The improved results obtained with such films are in part attributed to the use of better insulator layers as well as a high-temperature annealing of the ZnS film after vacuum deposition.

Similar to d-c powder layers thin-film phosphors exhibit a very sharp voltage threshold. When the threshold field is exceeded electrons trapped in the material are released and accelerated, causing collision, ionization, and excitation of the Mn luminescent centers. As in the case of powder-layer devices, *X-Y*-addressed multielement panels fabricated from such films have been used to produce television images and to display alphanumeric information. For example, panels with a diagonal of 16 cm containing 240×320 elements when operated at a frame rate of 30 Hz have produced television images with good gray scale and a highlight brightness of 20 fL (9).

Arrays of thin-film phosphor elements can also be used as memory devices (9) if the Mn content of the ZnS is increased from the amount normally used (about 1 percent by weight) to about 5 percent. If an a-c sustaining voltage just below the threshold (for example, 250 V rms, 5 kilohertz) is maintained across all the elements they will remain off. However, if the voltage across selected elements is raised during one half-cycle by the addition of a small "write" pulse they will be triggered to an "on" state and continue to emit light for an indefinite period. Since the "stored" level of light emission at different elements can be controlled by the magnitude of the write pulses, gray scale as well as on-off information can be stored. When desired either the entire array or selected elements can be switched off by interrupting for several cycles the sustaining voltage across these elements.

At present the storage mechanism in ZnS films is not clearly understood. However, it appears to be associated with a negative resistance effect produced by the increased Mn content. Somewhat similar to the a-c gas panel (described below) the storage action is attributed to the buildup and retention of charges at the phosphor-insulator interface each half-cycle. Although still in an experimental stage, storage panels of

this type are potentially useful for displaying stationary images with a very large number of picture elements, since writing can be accomplished at arbitrarily slow speeds and problems of flicker are avoided.

Although electroluminescent panels are promising for a number of information display applications they have the disadvantage of requiring high-voltage addressing circuits, particularly in the case of *X-Y* arrays where many drivers are required. This problem, however, is likely to be ameliorated as suitable low-cost integrated circuits are developed. Another problem is the low efficiency of electroluminescent layers (only a few percent of the efficiency of the best electron-bombarded phosphors) resulting in significant power dissipation in the panel and drive circuits. Aside from this, because of the limitations of present materials, the maximum brightness that can be expected from *X-Y* addressed panels with full television resolution is about 1/10 of that obtainable from cathode-ray tubes. Although attempts have been made to develop phosphors with colors other than the yellow-orange of ZnS:Mn the efficiency obtained is substantially lower than for this material.

Light-Emitting-Diode Displays

Unlike powder or thin-film electroluminescent layers which are microcrystalline in nature, light-emitting diodes are fabricated from single-crystal material in which *p-n* junctions are formed by the addition of suitable doping agents (10). Such diodes are a direct outgrowth of developments in semiconductor technology and the understanding gained of the detailed electronic processes occurring in such materials. Early studies of light emission from current flow through crystals were made by Lossev in 1923 using metallic contacts to naturally occurring SiC crystals. However, because of the low efficiency and the difficulty in obtaining reproducible results little interest was generated at the time. In 1962 strong interest in the subject arose as a result of the demonstration that infrared radiation with efficiencies as high as 50 percent could be generated in *p-n* junctions of gallium arsenide (GaAs). By 1968 diodes capable of emitting visible (red) light were introduced commercially fabricated from crystals of GaAsP. Since then improved materials with higher efficiency have been developed, emitting light with a variety of different colors. Light-emitting diodes have a number of characteristics

making them desirable for display applications. These include: (i) low-voltage operation allowing direct interfacing with semiconductor logic circuits, (ii) small size, (iii) long life (greater than 10,000 hours), (iv) high peak brightness, and (v) rectifying properties useful for *X-Y* addressing.

When a voltage is applied across a light-emitting diode in the forward or conducting direction electrons and holes present in the *n* and *p* sides of the junction, respectively, flow toward each other and, in the recombination processes occurring in the neighborhood of the junction, light is emitted. For the radiation to be in the visible range (as opposed to infrared) the energy difference between the holes and electrons (that is, the band gap of the semiconductor) must exceed about 1.8 electron volts. Although a number of luminescent materials satisfy this criterion (particularly those used for cathode-ray tube phosphors) the inability to fabricate *p-n* junctions in most of them precludes their use for light-emitting diodes. Materials of interest satisfying the requirements for light-emitting diodes are GaP, GaAsP, GaAlAs, GaN, and SiC. However, at present all commercial diodes are fabricated from crystals of the first two compounds.

The first commercial diodes were produced from $\text{GaAs}_{0.6}\text{P}_{0.4}$ deposited epitaxially as a thin layer on a GaAs crystal substrate. Using local diffusion techniques similar to those employed in making silicon diodes, *p-n* junctions were then formed. Corresponding to the band gap of $\text{GaAs}_{0.6}\text{P}_{0.4}$ (1.92 eV) an emission band of red light with a peak at about 650 nm is produced as a result of direct recombination of electrons and holes. Since the junction material as well as the GaAs substrate strongly absorb this radiation all of the light emitted in the direction of the substrate is lost. Because of the high index of refraction of the GaAsP, however, only light emitted toward the surface at an angle close to the normal (about 4 percent of the radiation in the forward direction) leaves the crystal, the remainder being reflected back. Frequently the diode is encapsulated in epoxy material shaped in the form of a lens. This concentrates the light in the forward direction and also doubles the light escaping since the index of refraction of the epoxy is intermediate between that of the GaAsP and air. Diodes of this material are particularly useful where a number are fabricated in close proximity on a single-crystal chip since the light produced by each diode is localized and can-

not spread to other areas. By taking advantage of this, single chips (for example, 0.2 inch high) with seven bar-shaped diode segments have been developed for numeric displays in pocket calculators.

Although diodes emitting light with shorter wavelengths, for example, yellow or green, can be made by increasing the phosphorus content of GaAsP (thus increasing the band gap), as the phosphorus content is increased beyond about 40 percent, a very rapid drop in efficiency occurs because of changes in the energy band structure which results in an increased number of the injected electrons and holes recombining non-radiatively to produce heat. It has been found, however, that the efficiency can be significantly increased by incorporating nitrogen atoms in the crystal which replace some of the arsenic or phosphorus (11). The nitrogen atoms in this case act as isoelectronic centers that can trap electron-hole pairs in an excited state. In recombining from this state these have a greater probability of producing light than by recombining through other processes. However, since some energy is initially given up by the electron-hole pair in the trapping process, the wavelength of the emitted light is somewhat less than that corresponding to the band gap of the material. The energy conversion efficiency of the nitrogen-doped diodes is, on the whole, comparable with that of red-emitting $\text{GaAs}_{0.6}\text{P}_{0.4}$ diodes. However, because of the increased sensitivity of the eye to green and yellow light compared to red, the luminous efficiency (lumens per watt) of the nitrogen-doped diodes is generally several times greater.

Three types of diodes with nitrogen doping have become important commercially: $\text{GaAs}_{0.65}\text{P}_{0.35}$, which emits orange light; $\text{GaAs}_{0.85}\text{P}_{0.15}$, which emits yellow light; and GaP, which emits green light. In the case of GaP (whose band gap is 2.25 eV), efficient diodes can also be produced if, instead of nitrogen, the material is doped with zinc and oxygen (a Zn atom replacing a Ga atom and an O atom replacing the nearest neighbor P atom). This Zn-O pair also acts to trap an electron-hole pair which may then recombine radiatively. However, because of the increased energy loss during trapping the light emitted is red with a spectral peak at about 700 nm.

In the case of nitrogen-doped materials the junction material is epitaxially grown on a GaP rather than GaAs substrate. Since the bandgap of the substrate as well as that of the GaAsP junction is greater than the energy of the

emitted photons, these materials are both transparent to the emitted radiation. By providing a reflecting surface at the rear of the substrate, light emitted into the substrate is reflected back, emerging at the sides and top surface of the diode structure and increasing its effective efficiency.

Except for GaP:Zn-O diodes (whose light output saturates with increasing current) the light output of the remaining diodes increases superlinearly with current. More efficient operation results, therefore, if the diodes are driven with periodic pulses of high current than with constant current. This characteristic, together with the short response time of junction diodes to current pulses (a small fraction of a microsecond), as well as their rectifying property which blocks current flow in the reverse (nonemitting) direction, makes them well suited for use in *X-Y* addressing arrangements. For example, using a matrix of 7×25 individual diodes, five-character displays are commercially available (using 5×7 diodes per character) in which successive rows or columns of diodes are simultaneously addressed. Recently display devices (16 by 12 cm in area) have been built which consist of an array of 320×240 individually selected green-emitting GaP diodes (each 0.3 by 0.3 millimeters in size). By addressing the diodes, one line at a time, television images with a highlight brightness of 70 fL have been demonstrated (12).

Although light-emitting diodes are useful for on-off indicators, small alphanumeric displays, and *X-Y* arrays of limited size, the cost of fabrication of large arrays of densely packed diodes as well as their high power dissipation (for example, about 0.1 watt/cm² required to produce a brightness level comparable to television screens) limits their usefulness for applications involving the display of complex images.

Gas-Discharge Displays

The fact that light can be produced by an electric discharge through a gas has been known for more than 200 years. Scientific interest in this phenomenon was stimulated in about 1856 by Geissler who fabricated glass tubes with electrodes sealed in at opposite ends and filled them with commonly available gases such as air, carbon dioxide, and hydrogen at low pressure. Although these tubes had a short operating life they were of technical interest for the study of the radiation spectra of different gases. In the early 1900's, soon after the

discovery of neon, elongated tubes containing this gas came into use for advertising signs. In such tubes almost all the light is produced by the "positive column," the luminous region starting a small distance from the cathode and extending almost to the anode. Soon after World War I small neon-filled bulbs became available commercially because of their usefulness as on-off indicators of 110- and 220-V power. However, because of their small electrode spacing (for example, several millimeters) they operate without a positive column, light being produced only from the "negative glow" region (also present in elongated tubes) immediately adjacent to the cathode. Despite the lower efficiency of this light generation (less than 1/10 of that from the positive column) most gas-discharge display devices, because of the small size of their elements, depend on this type of emission.

Gas cells have a number of desirable characteristics for display devices. Aside from their relatively simple structure, they can be made in arbitrary shapes and as small as 0.5 mm or less. Since a relatively sharp threshold voltage exists which must be exceeded to initiate a discharge, gas cells are well suited for use in *X-Y* addressing schemes. The fact that high peak brightness can be produced with short voltage pulses is also of importance for such addressing.

The gas-discharge cells used in all display devices are of the cold-cathode type, that is, the electron emission from the cathode required to sustain the discharge is not produced by heating but results from the transfer of energy from positive ions of the gas discharge to electrons at the cathode surface. Because of its chemical inertness and relatively high luminescent efficiency compared to other gases neon is almost always used. Generally, however, a small amount of a second inert gas is added to form a "Penning mixture" which allows operation at a reduced voltage (13). In the case of a discharge in pure neon, light is produced by excited atoms during electronic transitions to lower energy states, some of which are metastable. However, relatively few atoms acquire enough energy from the discharge to become ionized. By adding, for example, 0.1 to 1.0 percent of argon, a large fraction of the argon atoms become ionized by transfer of energy to them from the neon metastable atoms (whose energy is slightly higher than the ionization potential of the argon). Because of the increased ion generation the minimum voltage required to establish a discharge in such a mixture may be reduced, for example, to about

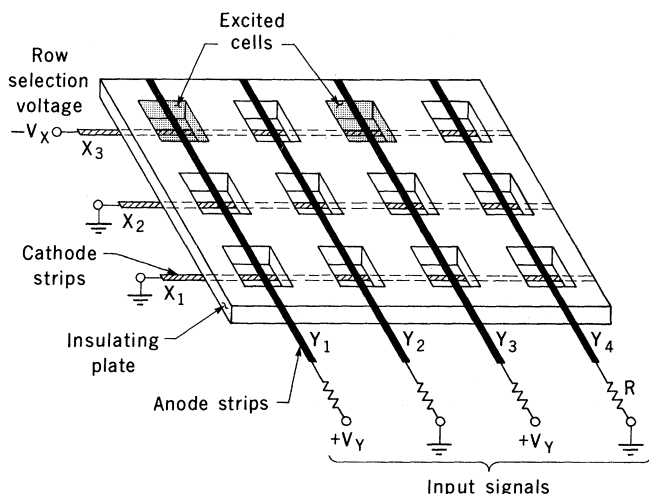


Fig. 2. Array of gas-discharge cells connected for X-Y addressing.

200 V compared to almost 300 V for pure neon.

In simple devices used for displaying a single character or numeral, a common anode may be used with a number of bar-shaped cathodes arranged in a suitable pattern (14). By applying sufficient voltage between the anode and selected combinations of cathodes, localized light emission is produced at these cathodes, allowing different characters or numerals to be displayed. For multicharacter or other displays involving a large number of elements, X-Y addressing is used as in electroluminescent displays to reduce the number of input leads and associated switching circuits (14). An example of such an arrangement is shown in Fig. 2. The individual cells here are defined by the holes in the insulating plate. In registry with the holes is a set of cathode strips on the lower surface of the plate. Running perpendicular to these is a set of anode strips on the opposite surface. Although not shown, it is assumed that the entire structure is contained between a pair of glass plates vacuum sealed at the edges and filled with gas at a low pressure, for example, 100 torr. In operation a pulse voltage, $-V_x$, is applied to one of the cathode strips (for example, X_3) while input signals in the form of pulse voltages, $+V_y$, are applied simultaneously to selected anode strips (for example, Y_1 and Y_3). Since the voltage sum $V_y + V_x$ is assumed to be greater than the threshold voltage, V_T , for initiating a gas discharge, light emission is produced at the two cells shown. Since the voltages V_y and V_x are assumed individually to be less than V_T no other cells of the array will fire. In a similar manner other rows of cells corresponding to cathode strips X_2 and X_1 can be addressed repetitively in rapid sequence to produce a flicker-free image. (To avoid excessive current flow through the "on" cells external lim-

iting resistors, R , are placed in series with the anode strips, as shown.)

As in the case of other X-Y-addressed luminescent displays, if the number of rows is increased the fraction of the time that a single row is on is decreased. To compensate for the reduced average brightness it is necessary to raise the addressing voltages to increase the peak currents through the cells. Unfortunately, this results in a rapid rise in cathode sputtering which limits the peak currents which can be used. In the sputtering process a metallic deposit from the cathode builds up on the walls of the cell as a result of bombardment of this electrode by energetic positive ions (14), causing short circuits or blocking the light transmission of the glass viewing surfaces. Although sputtering can be greatly reduced by the addition of a small amount of mercury vapor (a process not well understood) it is not believed practical to build displays with more than about 250 rows if acceptable brightness is to be obtained.

To overcome the brightness limitation experimental panels have been developed in which excited cells remain on continuously after being addressed, use being made of the fact that a gas discharge, once initiated, can be sustained by a somewhat lower voltage than the threshold voltage (14). If such a d-c sustaining voltage is maintained across all the cells of an X-Y-connected array, selected cells can then be triggered on by pulse voltages of reduced magnitude superimposed on the sustaining voltage. In a similar manner selected cells can be switched off by superimposing reversed-polarity X-Y pulses which momentarily lower the voltage of these cells below the minimum sustaining voltage. To limit the current flow through individual cells, however, it is generally necessary to provide a high-resistance element in series

with each cell, complicating the overall structure. Because of this, as well as addressing problems resulting from variations of firing and erasing voltage from cell to cell, interest in such devices is limited.

An alternative type of storage panel (15) which is in commercial use is shown in Fig. 3. Here the X- and Y-conductors are fabricated on the inner surfaces of two glass plates. These electrodes are then covered with a thin layer of glass (about $25\text{ }\mu\text{m}$ thick) so that they have no direct contact with the gas contained between the two plates. Because of the close spacing between the plates (for example, 0.1 mm) and the relatively high gas pressure (for example, >500 torr) of the neon-argon (or neon-xenon) gas mixtures used, the interaction between discharges at neighboring electrode crossovers is minimized allowing the cellular structure between the plates to be eliminated.

In operation an a-c sustaining voltage (usually in the form of rectangular pulses) is maintained between the sets of X- and Y-conductors. This voltage, capacitively coupled to the gas space is, by itself, insufficient to cause firing of any cell in the off state. However, if during a half-cycle, voltage pulses of suitable magnitude are applied to a selected pair of X-Y conductors a discharge can be initiated. This discharge will then quench itself within about a microsecond because of the buildup of charges on the insulating walls resulting from the current flow. Subsequent to this the cell will continue to fire on successive half-cycles since the voltage (of alternating polarity) built up on the walls during each half-cycle will add to the applied voltage of the next half-cycle. By triggering on selected cells in sequence a complete image can be stored. To switch a selected element off, appropriate X-Y signals are applied to the element (for example, during the off time between two half-cycles) to produce a weak discharge which causes the wall voltage to fall to zero rather than reverse polarity, preventing further firing of the cell by the sustaining voltage. In typical operation, an a-c sustaining voltage of about 100-V peak and 50 kHz is used, resulting in an average brightness of cells in the range of 30 to 75 fL. Commercial panels of this type have been built with 512×512 elements and about 21 by 21 cm in size. Experimental panels of larger size have also been built with 1024×1024 elements as well as with greater resolution (~ 3.3 lines per millimeter).

An important factor influencing the operation of the panels, aside from the

composition of the gas, is the nature of the insulating surfaces in contact with the gas. Although metallic sputtering does not occur, chemical and physical changes produced at the surface by ion bombardment may cause substantial changes in its secondary-emission coefficient which strongly influence the firing and erasing voltages of different elements, making it impossible to address all of the elements with *X-Y* signals of a given level. To minimize this problem the insulating surfaces are generally coated with a film (several micrometers thick) of evaporated or sputtered MgO which, in addition to being stable under ion bombardment, minimizes the addressing voltages required for the panel.

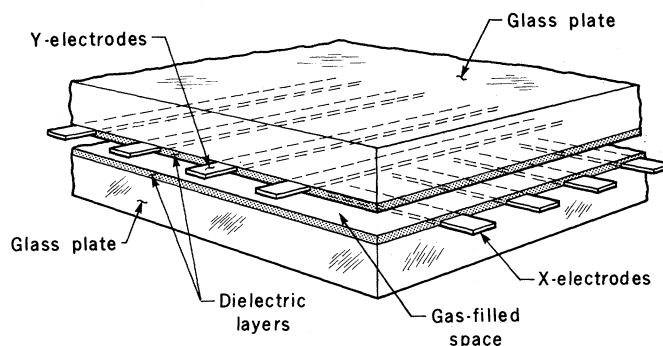
Advances in gas-discharge technology have also stimulated efforts to develop color displays for television applications. To obtain colors other than the orange-red of neon use is made of different photoluminescent phosphors deposited on the cell walls which can emit red, blue, or green light when excited by ultraviolet radiation. Instead of neon-argon, a gas mixture such as helium with 2 percent of xenon may be used whose discharge is rich in ultraviolet radiation. Although a number of cathode-ray tube phosphors are useful for this purpose, to obtain satisfactory life and improved efficiency at the short ultraviolet wavelengths of the gas discharge (100 to 200 nm), special phosphors have been developed such as $\text{BaAl}_{12}\text{O}_{19}:\text{Mn}$ for green emission and other europium-activated phosphors for the blue and red (16).

One of the limitations of gas panels, particularly for television applications, is their relatively low efficiency. In the case where the neon-argon discharge is viewed directly an efficiency of less than 1 lumen per watt is obtained (comparable to that of electroluminescent-layer and light-emitting diode displays). However, if photoluminescent phosphors are employed and a mixture of light from red, green, and blue cells is used to produce white light an efficiency of less than 1/10 of this is generally obtained. A panel 30 by 30 cm in size operating at the 100 fL brightness of commercial television would thus dissipate considerably more than 100 W.

Liquid-Crystal Displays

Unlike all of the previously discussed display media that generate their own light (referred to as emissive displays), liquid crystals fall into the class of display materials referred to as nonemissive since they control the transmission or re-

Fig. 3. Structure of a-c-type gas-discharge display panel.



flection of external light (usually ambient illumination). They are thus particularly useful for displays that must be viewed in high ambient light.

Liquid-crystal materials are a class of organic compounds which exhibit, within a certain temperature range of their liquid state, a number of optical and electrical properties characteristic of crystalline solids (17). Such materials were already the subject of scientific study before 1900, but it was not until the 1960's that interest in them for display devices arose when it was shown that an electric field applied across a thin layer could produce significant changes in light transmission with little power consumption. Since then, as a result of considerable materials and device research, liquid-crystal displays have come into widespread use in watches, pocket calculators, and a variety of electronic instruments.

The molecules of all liquid-crystal materials are generally elongated in shape. Because of this they are optically anisotropic, that is, the index of refraction is markedly different depending on whether the molecules are oriented parallel or perpendicular to the electric vector of a plane-polarized light wave (18). Fluids in the liquid-crystal state also may exhibit a large dielectric anisotropy particularly because of permanent (as well as induced) dipoles associated with the molecules. The latter property allows the alignment of the molecules to be changed by an external field while the former property makes possible a change in light transmission if a suitable optical arrangement is used.

Because of the forces between them the molecules of a material in the liquid-crystal state exhibit some form of long-range order in their alignment. Depending on the specific ordering relationship, different classes of materials exist, namely, nematic, cholesteric, and smectic. For almost all present display applications, however, nematic liquid-crystals are used. In these materials the molecules are aligned essentially parallel to each other but the location of their

centers is otherwise random. If the alignment direction is established at the boundary of the liquid (for example, at the surface of the glass plates confining the liquid-crystal material), the remaining molecules tend to assume the same alignment.

The most common displays in present use are the "twisted nematic" type. As shown in Fig. 4a, a layer of nematic material (about 10 μm thick) is contained between the transparent conductive surfaces of two glass plates. This structure is then placed between two polarizers. Before assembly the glass plates are specially treated to make the molecules at the surface align in a particular direction almost parallel to the surface of the plate. One method for accomplishing this is to evaporate a thin layer (about 100 angstroms thick) of SiO onto the glass surface at an oblique angle. Since the alignment directions of the two plates are set at 90° with respect to each other this causes a gradual twist in direction of the liquid-crystal molecules between the plates as shown. If the input polarizer is oriented, for example, parallel to the alignment of the liquid-crystal molecules at the top plate, the plane of polarization of the light passing through the liquid crystal will be rotated by 90° because of the gradual twist of the liquid-crystal molecules. This light will then pass through the analyzer adjacent to the lower plate whose orientation is set perpendicular to the polarizer.

Since liquid-crystal molecules are used that have a strong dipole moment in the axial direction, if an a-c voltage (for example, 2 to 3 V rms) is applied across the cell, the molecules (except those held by surface forces at the glass plates) will to a large degree orient themselves perpendicular to the glass surfaces as shown in Fig. 4b. In this orientation the liquid-crystal layer can no longer produce a rotation in the polarization plane of the light, causing it to be blocked by the analyzer. In most display devices the ambient light itself is used as the source and, instead of viewing the changes in transmitted light, a reflector is placed at

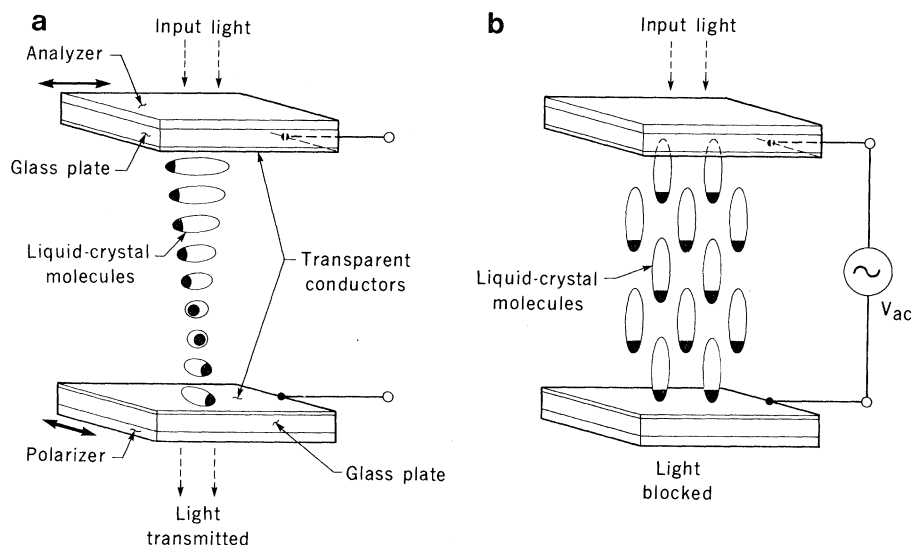


Fig. 4. (a) Twisted-nematic liquid-crystal cell with no voltage applied. (b) Orientation change of liquid-crystal molecules produced by applied a-c voltage.

the output to return the light back through the cell, thus permitting viewing from the input side.

Many of the liquid-crystal materials found useful in early device work have a molecular structure whose inner portion consists of two aromatic rings with an additional central group linking them together (19). One important class, the Schiff base materials (characterized by the $-\text{CH}=\text{N}-$ central group) was studied extensively. The first compound of this class which could be used at room temperature (commonly known as MBBA) is in the nematic liquid-crystal state over the temperature range of 22° to 48°C . Another compound of this class (known as EBBA) is nematic over the range of 35° to 77°C . However, by mixing the two compounds in the correct proportion eutectic mixtures have been reported (19) whose nematic range extends from 0° to 60°C . For use in twisted-nematic displays, Schiff base and other materials have been developed with an end group (such as $-\text{C}\equiv\text{N}$) attached to one of the aromatic rings which provides a strong axial dipole.

Materials of the above types suffer from decomposition in the presence of small amounts of water or when exposed to ultraviolet radiation, resulting in the breaking of the bonds between the two aromatic rings. In the past few years, however, new materials have been developed such as the biphenyls in which the aromatic rings are directly linked, making the molecules extremely stable in the presence of moisture, air, and light (20). These also may have a CN group attached at one end to form a strong axial dipole and, depending on the particular alkyl or alkoxy group attached at the oth-

er end, allow different operating temperature ranges to be obtained. By using two or more compounds of this type, eutectic mixtures have been obtained that are nematic over a temperature range of -10° to 60°C . (Recently, new materials such as phenylcyclohexanes have been developed with comparable stability and temperature range.) It is of interest that because of the chemical stability and long life of present liquid-crystal materials (which may be considerably greater than 10^4 hours) the life of display devices is frequently limited by the deterioration of the plastic polarizing sheets usually employed which tend to degrade under conditions of high temperature and humidity.

To avoid electrolytic decomposition of liquid-crystal cells, it is usual to apply a-c voltage (for example, 100 Hz) rather than d-c. Because of the high resistivity of the materials (greater than 10^{10} ohm-cm) the power consumption is very small, being less than 1 microwatt per square centimeter (several orders of magnitude lower than for luminescent displays). Liquid-crystal materials are thus ideally suited for portable, battery-operated devices. An important limitation of liquid-crystal displays is their relatively slow response, the turn-on and turn-off times both being of the order of 0.1 second at room temperature (21). Because of the increasing viscosity of the material at low temperature, the turn-off time at -10°C may be about 1 second. At a given temperature the turn-on time varies inversely as the square of the applied voltage. The turn-off time, which depends on the realignment forces between the molecules, increases with the square of the distance between electrodes.

To eliminate the polarizers and provide a wider viewing angle considerable present effort is being directed toward liquid-crystal materials in which a pleochroic dye is dissolved (20). The elongated molecules of such a dye absorb light over a broad spectrum if they are oriented parallel to the electric vector of plane-polarized light but are relatively transparent if they are oriented perpendicular to this vector. Since the dye molecules tend to align in the same direction as the liquid-crystal molecules their orientation can be controlled by electric fields which act on the liquid-crystal material. In the preferred arrangement the dye molecules are incorporated in a cholesteric-type of liquid crystal whose molecules are made to align parallel to the cell walls. Unlike twisted-nematic cells, however, the molecules of the cholesteric material have an intrinsic twist angle which may be much greater (for example, several complete cycles instead of 90°) determined by the thickness of the layer rather than the orientation of the glass plates. In this state the dye molecules, oriented in all directions, absorb unpolarized light. If a voltage is applied, as in the case of the twisted-nematic cell, the liquid-crystal molecules (together with the dye molecules) orient themselves perpendicular to the glass surfaces, greatly reducing the light absorption. To obtain satisfactory operation, however, it is necessary to use dye molecules that are strongly oriented by the liquid crystal and are chemically stable. Very recently anthraquinone dyes have been reported which satisfy these conditions well (20).

Attempts to use X-Y addressing techniques for liquid-crystal displays have resulted in limited success. Aside from the threshold voltage not being very sharp, it varies with viewing angle and temperature. In addition, associated with their relatively sluggish response, liquid-crystal cells respond to the integrated effect of repetitive voltage pulses (in particular the rms voltage) rather than the peak value (20). In an X-Y-addressed array the response of unselected elements is thus almost as great as for selected elements since unselected elements are repetitively excited with "half-select" voltages (that is, either X or Y voltages alone), resulting in very low image contrast. With twisted-nematic cells X-Y-addressed arrays having good contrast over an acceptable viewing angle have not yet been developed with more than about ten rows. However, if collimated light can be employed, such as in projection systems,

other optical effects in liquid crystals can be used whose threshold is much sharper, allowing images to be obtained from arrays with up to several hundred rows.

To overcome the *X-Y* addressing limitations of liquid crystals other approaches are being investigated in which a highly nonlinear resistive element (22) or a field-effect transistor is incorporated at each picture element to prevent voltage from appearing across unselected elements. In these arrangements a small capacitor is usually incorporated at each picture element as well. This is charged in accordance with the peak value of the *X-Y* signal voltages and then allowed to discharge through the relatively slow-responding liquid-crystal element over an extended time.

Miscellaneous New Displays

Aside from the primary display media discussed above, several other types of displays are being investigated, particularly those based on electrochromic and electrophoretic phenomena. Both of these are non-emissive, with interest in them stemming from their relatively low power consumption, memory effects, wide viewing angle, and usefulness at high ambient light levels.

Electrochromic displays make use of a material whose color can be changed reversibly by passing an electric current through it (23). Such coloration processes involve either a valence change of one of the constituent ions or in the formation of a color center associated with a lattice defect. One material that has been studied is deheptyl viologen dibromide, which is colorless in an aqueous solution. If voltage is applied across a cell containing this material an insoluble purple compound is formed on the cathode surface. Another material extensively studied is tungsten oxide. If a thin film of this material is coated on the transparent cathode of a cell containing an electrolyte that can supply H^+ ions (for example, H_2SO_4) the film will change from a transparent to a blue-colored state as a result of current flow through the cell. In this process it is believed that a tungsten bronze, H_xWO_3 ($x < 0.5$) is formed as a result of H^+ ions being injected into the film from the electrolyte together with electrons from the cathode. More recently, electrochromic action has been reported in iridium oxide films (24), the coloration here being attributed to the injection of hydroxyl (or other negative) ions from the electrolyte coupled with the extraction of electrons from the film by the anode. In the case of

tungsten oxide and iridium oxide films, attempts have been made to replace the liquid electrolyte with a solid electrolyte or superionic conductor. Although some success has been achieved, with present materials limited life or reduced speed of response is obtained.

Electrochromic displays, like liquid-crystal displays, have the advantage of low-voltage operation (about 1 to 2 V). The switching time (dependent on the material and current density used) is of the order of 0.1 second. Although cells have been reported capable of 10^7 switching cycles, one of the problems encountered is deterioration due to unwanted electrochemical side effects, especially if the applied voltage is raised beyond a certain level. Typically an integrated charge transfer of several millicoulombs (or more) per square centimeter is required to produce a change in coloration, the power consumed in switching being several orders of magnitude greater than for liquid crystals. It should be noted that, because of the electrochemical processes occurring, a reverse voltage is built up during the coloration process. If the cell is short circuited the reverse current flow will cause decoloration (a situation which may be undesirable in *X-Y* addressing circuits). However, if the cell is maintained in the open-circuit condition after coloration it can remain in this state for hours or longer, thus providing a memory effect.

Electrophoretic displays make use of a thin layer of dyed fluid in which pigment particles of a strongly contrasting color or reflectivity are suspended (25). Depending on the materials used, as well as charge-control agents added, the particles may acquire either a positive or a negative charge with respect to the liquid. If a layer of such fluid is confined between two parallel electrodes (for example, 50 μm apart) and a d-c voltage (for example, 100 V) is applied, the particles will be drawn to one electrode, building up a coating on the surface. If this electrode is transparent, the color observed will be primarily due to the reflectivity of the particles (for example, yellow or white). After removal of the voltage the cell may remain in this state for hours. However, if a reverse voltage is applied the particles will be drawn to the opposite side of the cell and the color observed through the electrode will be that of the dyed fluid (for example, black or blue) which hides the particles.

Because of their high index of refraction and good light-scattering property titanium dioxide particles (which appear white) have frequently been used. To avoid sedimentation from occurring be-

cause of their high density compared to available fluids the particles have in some cases been coated with a resin to reduce their average density. Other particles that have been used are organic pigments, such as Hansa yellow and Diarylide yellow, whose density can be matched by a mixture of suitable fluids. The fluids used should have a high resistivity (for example, 10^{12} ohm-cm), should be chemically stable and, to enable high particle mobility, should have high dielectric constant and low viscosity. Some fluids that have been used are xylene, perchloroethylene, and trichlorotrifluoroethane.

To obtain satisfactory life times it is important to prevent flocculation or agglomeration of the particles, especially when they are compacted at the electrodes. Although to a limited degree this is prevented by the mutual repulsion of the charged particles, generally steric stabilizers are added to the solution. These provide long-chain molecular groups that attach to the particles and protrude outward, thus preventing the particles from approaching too closely.

To produce switching, relatively little integrated current flow is required (about $0.1 \mu C/cm^2$), an advantage for low-power applications. The switching time is typically in the range of 10 to 20 msec, for a given material being proportional to the square of the electrode spacing and inversely proportional to the applied voltage. Because of their poor threshold characteristics, *X-Y* addressing techniques cannot be used effectively with electrophoretic cells unless some additional circuit component is added at each picture element. However, encouraging results have been obtained with cells incorporating an additional control-grid electrode which prevents particle migration unless both *X* and *Y* voltages are simultaneously applied (26).

Conclusion

To satisfy the great variety of applications emerging for displays (covering the gamut from large-screen television to small watches) a continually widening circle of diverse phenomena and new materials is being explored. The field of display technology is thus more a collection of somewhat unrelated topics than a single cohesive subject. Although the performance of different display devices can be evaluated in terms of a number of objective criteria, for example, speed of response, power consumption, or brightness, a comparison of displays on this basis alone may lead to simplistic and er-

roneous conclusions. In many cases other factors such as flicker, uniformity of elements, variation of contrast with viewing angle, or color may be of comparable importance, requiring subjective judgments to assess their effects. Despite the different immediate and specific goals of the various display technologies, in many cases they share a common long-term goal, namely the achievement of a level of performance comparable to that of the cathode-ray tube. Given the present limitations of these technologies, however, this goal is not likely to be achieved in the next few years but rather in an evolutionary manner extending over a much longer period.

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Transmission electron micrograph showing the magnetic domain structure (meandering strips) in a thinned samarium —→ thulium iron oxide garnet crystal. Electrons in the microscope are deflected by the Lorentz force due to the magnetization distribution across the domain walls that define the domains. Submicrometer domains (about 0.5 micrometer wide) and actual wall structure, both unresolvable by light optical methods, are revealed. [S. Herd, IBM Thomas J. Watson Research Center, Yorktown Heights, New York]