

# A Novel Electrophotographic System

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A novel electrophotographic system is described which consists of a thin film of a transition metal oxide and a thin film photoconductive layer sandwiched between a pair of electrodes. When an electric field is applied across this composite structure and an optical image is projected on it, the resulting modulation of the conductivity pattern in the photoconductive layer causes a similar coloration pattern in the oxide layer, thereby forming a visible image. The formation of color centers and the associated optical and electrical properties are discussed.

## Introduction

During the past several years we have witnessed a phenomenal growth in development of new image forming devices which employ a variety of optical and electrical properties of solids.<sup>1-3</sup> The most remarkable progress has been made in the field of electrophotography. Basically, all electrophotographic processes involve the formation of a latent image on a photosensitive medium, followed by development of the latent image into a visible image. The work that is described in this paper, although adhering to the same general principle, has several unique features.

The underlying principle of our imaging device involves the formation of color centers in thin films of certain transition metal oxides by the application of an electric field. Coloration occurs at a critical field strength; intensity of coloration is proportional to the applied field and length of exposure. A thin film of these materials, henceforth referred to as electrochromic, coupled with a photoconductive film, forms a solid state imaging device. When an image is projected on the photoconductive layer, local variation of the conductivity causes a corresponding distribution of potential across the electrochromic film. If the voltage across the electrochromic layer in the dark is maintained below the critical voltage necessary for coloration, exposure to light of an energy corresponding to the response frequency of the photoconducting layer will cause the exposed region to exceed the critical voltage, and coloration results in the electrochromic film, thereby forming a visible image. The device is analogous to the well-known El-Pc system<sup>4</sup> except that the electroluminescent material is replaced by an electrochromic film.

## Properties of Electrochromic Films

Before discussion of the imaging process itself, it is useful to describe the phenomena of color-center formation in thin films of metal oxides. It has been reported<sup>5-7</sup> that thin films of  $\text{WO}_3$  and  $\text{MoO}_3$  form color centers when exposed to uv radiation in the region of fundamental absorption edge. The same types of color centers are also formed when a dc electric field ( $\sim 10^4$  V/cm) is applied across the film at room temperature. The phenomenon is demonstrated in a thin film of  $\text{WO}_3$  ( $\sim 1 \mu$  thick) with a pair of evaporated gold electrodes on the surface as shown in Fig. 1. On applying 1400 V across the film, the coloration begins at the cathode and slowly propagates toward the anode. Within half an hour the entire interelectrode spacing (2.5 mm) is completely colored except for a very narrow region near the anode. The result obtained on one such film is shown in Fig. 1. On reversing the polarity of the applied field, the color-center cloud migrates back toward the new anode and bleaches at the same time. On continued application of the field, coloration appears at the new cathode, and the process can be repeated many times. The behavior of the color centers with regard to the formation and migration in an electric field is essentially the same as that of color centers observed in alkali halides<sup>8</sup> and  $\text{TiO}_2$  (Ref. 9) single crystals at elevated temperature. The coloration in these electrochromic films is a sensitive function of a number of physical parameters such as electrode materials, impurities, and ambient condition.

The optical absorption spectrum of the electrically colored film is almost identical to the spectrum obtained on an uv irradiated sample.<sup>5,6</sup> The spectrum consists of a broad absorption band that covers almost the entire visible and near ir region with peak position near 8000 Å. The color centers can be bleached by heating in oxygen at 300°C, but once the film is bleached in oxygen it cannot be colored again. As-

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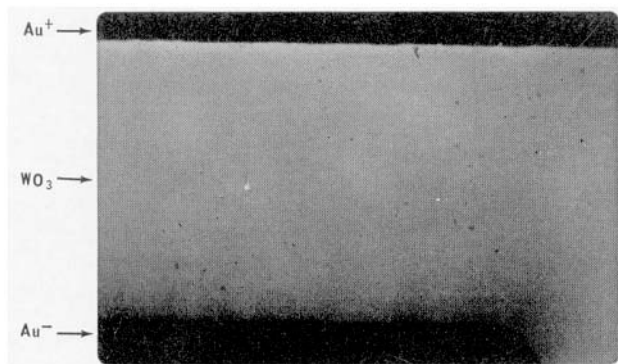


Fig. 1. Electric field induced coloration in a thin film of  $\text{WO}_3$  with surface electrode structure.

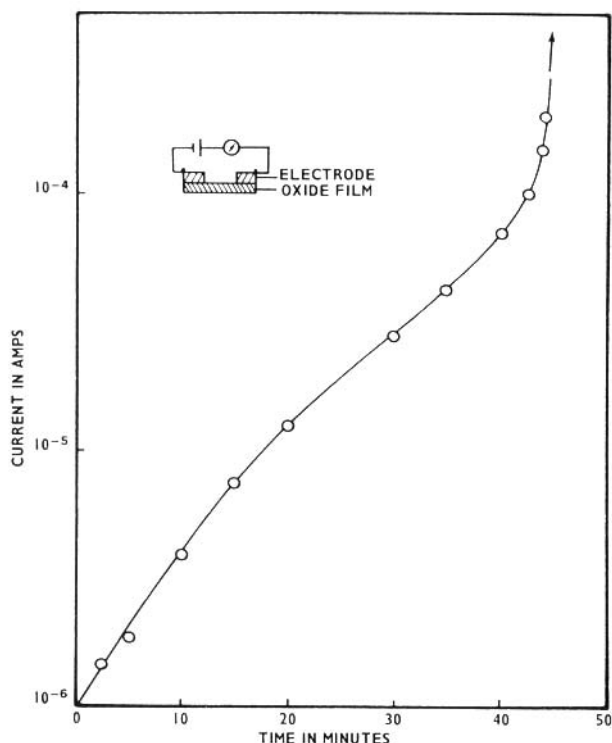


Fig. 2. The change in electrical conductivity as a result of coloration of a  $\text{WO}_3$  film.

sociated with the color-center formation there is an increase in dark conductivity of the electrochromic film. This provides a useful means of studying the extent of coloration. The conductivity increases by several orders of magnitude. The change in electrical conductivity as a result of coloration of a  $\text{WO}_3$  film is shown in Fig. 2. The conductivity increases by a factor of 100, after which dielectric breakdown occurs, and this is typical of all samples studied so far.

### Sandwich Type Electrochromic Layer

So far, we have been discussing the coloration phenomena in the electrochromic film by using an electrode structure deposited on the film surface as shown in Fig. 1. Because of the geometry involved in such a

system, it was necessary to apply  $2 \times 10^3$  V to produce a field strength of  $\sim 10^4$  V/cm required for coloration. It is evident that, by making a sandwich structure, it is possible to obtain the same field strength applying 1 V across a  $1\text{-}\mu$  thick film.

A sandwich structure was prepared by the vacuum evaporation of the oxide film ( $\sim 1\text{ }\mu$  thick) on NESAG glass, followed by evaporation of a thin transparent gold film on top of it. Using gold as the cathode and applying 2 V across the film, the oxide layer developed a deep blue coloration in a few seconds. Figure 3 shows a sandwich structure before and after coloration.

A slowly varying potential was applied across this structure, and the current-voltage characteristic was plotted on an X-Y recorder. The complete I-V curve with different modes of polarity is shown in Fig. 4. With gold as cathode there is a very slow increase of current up to 2 V, followed by a rapid increase of current and the appearance of coloration in the electrochromic layer [cf., Fig. 4 curve (a)]. The I-V curve after 1 min of coloration is shown in Fig. 4(b). With progressive coloration, there is a gradual decrease of the threshold voltage for rapid current rise, and as the coloration reaches the saturation value the I-V curve takes the form shown in Fig. 4(c). The structure behaves like a rectifying diode with coloration occurring in the reversed bias condition. No bleaching occurs on reversing the polarity. Clearly, there exists a threshold voltage ( $V_t$ ) for coloration, and if this is taken as a measure of barrier height at the metal oxide contact, it is evident that it decreases with increasing coloration.

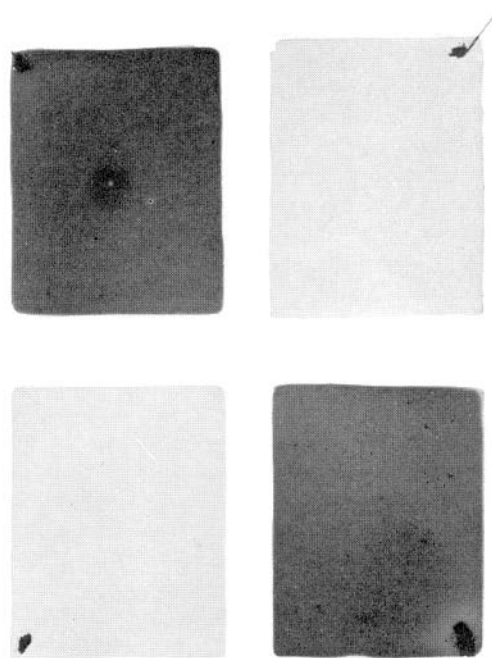


Fig. 3. Electrical coloration in a sandwich structure of  $\text{Au-WO}_3\text{-SnO}_2$ .

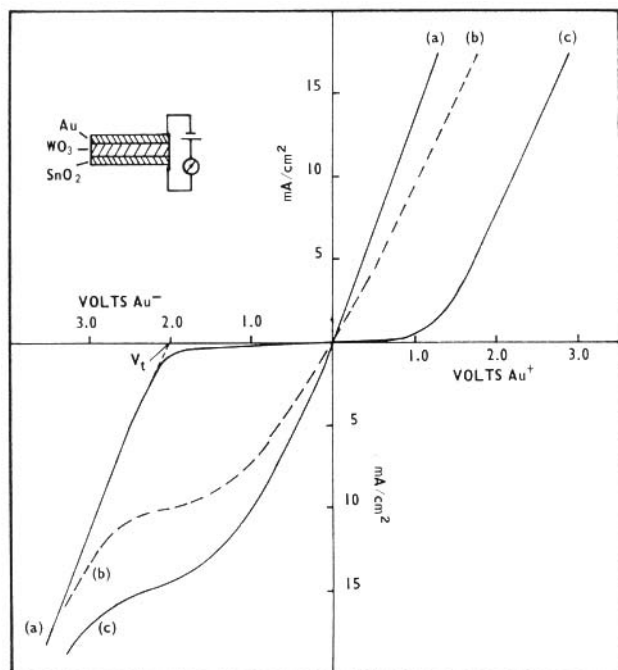


Fig. 4. The current-voltage characteristic of a sandwich structure of Au-WO<sub>3</sub>-SnO<sub>2</sub>.

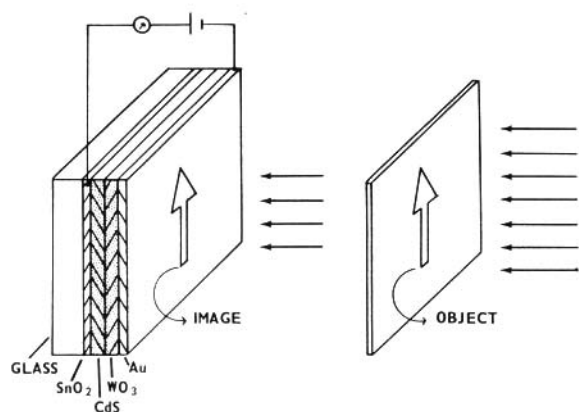


Fig. 5. Diagram of an electrophotographic arrangement.

### Image Recording in the Electrochromic Film

We can now describe a process for making an image in an electrochromic film. Figure 5 shows the principal elements of the proposed electrophotographic structure. A thin film of CdS, about  $0.5 \mu$  thick, is vacuum deposited on a carefully cleaned Nesa glass substrate. Deposition is carried out at  $10^{-5}$  mm pressure while maintaining the substrate at  $150^\circ\text{C}$ . The CdS film thus obtained is quite conductive, and its photocurrent/dark current ratio is 2.5. The film is then heated in air at  $350^\circ\text{C}$  for 16 h so that the dark conductivity of the film decreases by several orders of magnitude and becomes less than the conductivity of the electrochromic film. At the same time, the photo/dark current ratio increases from 2.5 to 300. A thin film of an

electrochromic oxide, also  $0.5 \mu$  thick, was then evaporated on the CdS film at  $100^\circ\text{C}$ . Finally, a transparent gold electrode layer ( $100 \text{ \AA}$ ) was deposited on the oxide layer to complete the sandwich structure.

An optical image of the object to be photographed was projected on the photoconductive film using a 54-W tungsten filament light source. On subsequent application of a dc field of 3 V across this structure, a visible image could be developed in 1 sec; the initial current flow through this structure under these conditions was 10 mA. A typical electrophotographic image, recorded by making a contact print through an ordinary photographic negative by 1-min exposure, is shown in Fig. 6. The sharpness of the image is readily visible. On enlarging the image with an optical microscope to magnification up to  $150\times$ , no granular structure or distortion of the image was revealed. A suitable apparatus for recording optical images by the projection of photographic negative can easily be constructed from an ordinary photographic enlarger.

The stability of the resulting image varies from semipermanent to permanent depending upon the choice of the appropriate electrochromic material. Some of these semipermanent systems exhibit a memory effect. For example, it has been observed that, even though the image fades away, it could be restored again by subsequent exposure to visible light and an electric field. The shelf life for one of these electrophotographic systems was tested over a period of three years and was found to be still operative.

Since the conductivity of the electrochromic layer increases with coloration, the optical density of the resulting image can be determined by monitoring the current



Fig. 6. Photograph of an image recorded on the electrophotographic structure.

flow through the system. In addition, the device has the property of providing a built-in mechanism for dodging. The induced absorption band in the electrochromic layer overlaps the photocurrent spectrum, which gives an intensity variation of the projected image on the photoconductive layer, resulting in an alteration of the tonal scale of the electrochromic image.

For operation of a device of this type in which the photoconductive and electrochromic layers are connected in series, it is important to have proper impedance matching. The problem encountered in this case is essentially similar to that of EL-Pc system which has been described in detail by Nicole.<sup>3</sup> An analytical determination of the input-output characteristic of such a device has not been done as yet. However, a system of this kind should have considerable amplification which would, of course, depend on both the conversion efficiency of light to current of the photoconductor and also on the conversion efficiency of current to density of color centers in the electrochromic layer.

### Information Recording by Electrography

The electrochromic phenomenon outlined can be utilized for electrographic printing that has considerable use in data printout systems. A visible image pattern can be formed on an electrochromic film deposited on a conducting substrate by means of a pointed probe electrode that is maintained at a negative potential. The pointed cathode produces a strong field gradient which results in instantaneous coloration of the electrochromic film.

### Conclusions

The electrophotographic process described is simple and requires no special apparatus. The process has the potential of fulfilling the basic criteria of an ideal photographic system such as amplification, dry processing, sensitivity, resolution, and contrast. One of the major limitations of this process at this stage is speed, which undoubtedly can be improved. Advantages of the system are: (1) single step operation to form a visible image, (2) insensitivity to light in the absence of an electric field, (3) ultimate resolution on a molecular scale. Potential applications of this system may be in high resolution photography, photocopying, microrecording, information storage and display, ir and x-ray imaging, image intensifier, and the like.

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