CHARGING PROPERTIES OF AMORPHOUS SELENIUM FILMS RELEVANT TO XEROGRAPHIC USE

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ABSTRACT

Measurements of the basic properties of amorphous selenium films relevant to xerographic use were carried out using special apparatus built in the laboratory. The samples for study were prepared in the laboratory and consisted, in each case, of an aluminum plate on which a thin oxide film was formed, followed by the deposition of a 50 micrometer layer of amorphous selenium by evaporation at a substrate temperature near 50 °C. The free selenium surface of the sample was then charged to a positive or negative potential from a corona discharge and the acceptance voltage and voltage decay rate in darkness and the residual voltage after illumination were measured. The effect on these quantities of varying the selenium layer thickness, its deposition temperature and deposition rate was determined along with the effect of using selenium containing different concentrations of chlorine. The results point to a dark decay process controlled by injection of carriers from the substrate for undoped selenium and controlled by charge depletion resulting from the emission of carriers from discrete centres in chlorine-doped selenium. Different methods of oxidation were used to form the thin aluminum oxide film, which acts as a blocking layer between the selenium and the aluminum sudstrate. These methods were evaluated in terms of the xerographic properties of the samples. The thicknesses of the oxide films were determined from capacitance measurements made on samples prepared using evaporated metal contacts without the selenium layer.

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RESUME

On a mesuré les propriétés xérographiques élémentaires du sélénium amorphe en couches minces à l'aide d'un appareil spécialement adapté construit dans ce laboratoire. Les échantillons étudiés ont été fabriqués dans ce laboratoire et sont constitués dans tous les cas d'une plaque d'aluminium sur laquelle on a formé un film mince d'oxyde avant d'y déposer par évaporation une couche de sélénium amorphe d'environ 50 microns le substrat étant maintenu à une temperature d'environ 50 °C. La surface libre du sélénium a alors été portée à un potentiel positif ou négatif par une décharge électrique par effet de couronne et on a mesuré la tension admissible et la vitesse de décroissance de la tension dans l'obscurité ainsi que la tension résiduelle après illumination. On a étudié l'influence sur ces quantités de l'épaisseur de la couche de sélénium ainsi que de la température et de la vitesse d'évaporation. Les effets produits par l'utilisation de sélénium contenant différentes concentrations de chlore ont également été déterminés. Les résultats ont montré que le processus de décroissance de la tension dans l'obscurité est contrôlé par l'injection de porteurs de charge provenant du substrat dans le cas du sélénium non dopé et par appauvrissement de charge dû à l'émission de porteurs par des centres discrets dans le cas du sélénium dopé au chlore. On a

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utilisé différentes méthodes d'oxidation pour former le film d'oxyde d'aluminium qui se comporte comme une couche de blocage entre le sélénium et le substrat d'aluminium. L'influence de la méthode d'oxidation sur les propriétés xérographiques des échantillons a été évaluée. L'épaisseur des films d'oxyde a été déterminée à partir de mesures de capacité effectuées sur des échantillons sans couche de sélénium sur lesquels on a évaporé des contacts métalliques.

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CHAPTER 1 INTRODUCTION

The dry electrostatic xerographic process is now extensively used for photocopying documents and for medical X-ray graphic recording. A number of photoreceptor materials are in use for such applications but materials based on amorphous selenium are still widely employed.

Much empirical knowledge has been acquired on the technology of photoreceptor materials based on amorphous selenium but most of it is unpublished and is only known to those companies and organizations skilled in the art of xerography. Much of this information is of a proprietary nature and would not be available to the public. Accordingly, the only way to acquire experience in this art is actually to work in the field in the laboratory using what published material is available. In this way, some of the requirements of the selenium receptors for xerographic use can be determined. It has therefore been the objective of the present work to acquire as much knowledge as possible, within the resources of our laboratory, of the xerographic properties of amorphous selenium. It is hoped that this work will lead to new information and that the experience gained may be helpful in

providing useful assistance to those engaged more directly in the supply of selenium for xerographic use.

It may be helpful to review firstly the basic photocopying process $[1]^{-[4]}$ as illustrated in Fig.1.1. First the photoreceptor (selenium) surface is charged from a corona discharge in darkness (Fig.1.1(a)). For the sake of being definite, this surface charge is taken to be positive, although negative charging is also possible. Then the surface is illuminated, with light of wavelength less than the bandgap value, projected on its surface as an image from the document to be copied (Fig.1.1(b)). Where the light is blocked by black areas of the pattern, the charge on the photoreceptor plate remains but where the light reaches the photoreceptor the surface charge leaks away by photoconduction to the conducting substrate. A powder mixture called developer, consisting of toner and carrier, is then applied to the plate (Fig.1.1(c)). The toner particles of this powder are pulled away from the carrier and adhere to the charged regions of the photoreceptor plate but do not stick to the uncharged regions. Next a sheet of white paper is placed over the powder image and the back of the paper is charged positively (Fig.1.1(d)). The paper with the toner pattern is then removed from the plate and heated so that the ink of the toner is baked in to produce a copy of the original (Fig.1.1(e)). The photoreceptor plate is then cleaned by a specially designed non-woven cloth to remove all residual toner and fully discharged by strong illumination so that the plate may be used again (Fig.1.1(f)).

The structure of a photoreceptor plate is shown schematical-

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ly in Fig.1.2^{[1],[2]}. The basic photoreceptor layer (selenium in

the present case) may be covered on its top surface by a thin film of material to inhibit the loss of charge to the air. The photoreceptor itself is deposited on a conducting substrate (aluminum in the present case), which serves to supply the discharging current during illumination. Between the substrate and the photoreceptor is another film of material, whose purpose is to block the entry of carriers into areas of the plate which are not illuminated. Aluminum oxide is often used as the material in this interfacial layer. Sometimes there is a double photoreceptor layer to assist the xerographic process.

In the present thesis, xerographic measurements were made on samples consisting of amorphous selenium deposited on polished aluminum with an interfacial layer of aluminum oxide. During the deposition of the selenium by evaporation, the substrate was maintained at a temperature low enough to prevent crystallization but high enough to yield material with suitable xerographic properties. The selenium thickness was usually about 50 micrometers. The xerographic measurements on the samples consisted of charging the samples and determining values of acceptance voltage, dark decay rate and residual voltage after illumination. These terms will be explained in chapter 4. The effect on these quantities was studied in the first part of the investigation with variation of selenium thickness, deposition temperature, deposition rate and the chlorine content in the selenium. In the second part of the investigation, different methods were used to form the aluminum oxide blocking layer between the selenium and

the aluminum substrate. Then the xerographic properties were measured on standardized selenium layers with the differently prepared interfacial oxide films and the influence of these was determined. As will be seen, this interfacial layer affects particularly the dark decay rate.

To demonstrate the photocopying action in the films prepared in this laboratory, a very simplified process was used and this is described in the Appendix.

Much useful experience was gained in this work in the art of making structures giving good xerographic performance using amorphous selenium and some important results were obtained. Never-the-less, the work must be considered to be only a beginning, since other xerographic parameters need to be studied as well as a greater range of selenium-based materials.

The structure of the thesis is as follows. Firstly, some theoretical considerations are presented in chapter 2 to describe the dark decay process. Details of sample preparation are given in chapter 3 and the measurement methods are described in chapter 4. The results of the variation of selenium thickness, deposition temperature, deposition rate and chlorine content in the selenium are presented in chapter 5. The work done on differently prepared aluminum oxide inter-layers is reported in chapter 6. Finally, the main conclusions and future work are given in chapter 7.



Fig.1.1 Basic steps in Xerography. (From Schaffert^[5].)



Fig. 1.2 Structure of Xerographic Photoreceptor^[1].

CHAPTER 2 THEORETICAL CONSIDERATION OF DARK DECAY

2.1 INTRODUCTION

The xerographic process involves corona charging of the photoreceptor surface, slow dark decay of the charge, illumination with light resulting in a fast charge decay and finally a slower decay to a residual charge. These processes are complex and a full theoretical treatment^{[5]-[14]} of them is not appropriate here. However, it is helpful to consider theoretically the process most relevant to the experimental work in this thesis, which is dark decay. Therefore, this chapter presents some theoretical considerations of the decay of voltage resulting from injection from the base, limited by trapping of the carriers and by the emission of carriers from discrete centres distributed in the bulk of the receptor layer. The theoretical treatments presented, however, are only for specific cases, since a fully comprehensive treatment of even dark decay lies outside the scope of this thesis.

2.2 INITIAL FREE CARRIER DEPLETION

Although amorphous selenium as used in xerography has a very high electrical resistivity (10^{14} ohm cm^{[1],[5]}), it does have a small concentration of free holes (of the order of 10^6 cm³). When a charge (taken to be specific as positive) is applied to the top surface of the selenium layer, these carriers are quickly swept out into the conducting substrate. The transit time for this can be estimated as follows.

Suppose a positive surface charge of σ per unit area is applied to the free selenium surface, yielding a potential V at the surface with respect to a grounded conducting substrate (Fig.2.1). The mobile holes will experience an electrostatic field E, which if uniform, is V/L, where L is the thickness of the selenium layer. The hole



of the selenium layer. The holes are then swept across L in a transit time t_t given by:

$$t_{t} = \frac{L}{\mu_{p}E} = \frac{L}{\mu_{p} V/L} = \frac{L^{2}}{\mu_{p} V}$$

where $\mu_{\rm p}$ is the mobility of the holes. Taking the values L=50 μ m,

V=800 volts and $\mu_p=0.1 \text{ cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$, t_t is calculated to be:

$$t_{t} = \frac{(50 \times 10^{-4})^{2}}{0.1 \text{ cm}^{2} \text{ volt}^{-1} \text{ sec}^{-1} 800 \text{ volt}} = 3.125 \times 10^{-7} \text{ sec} \approx 0.3 \ \mu \text{sec}$$

Thus, compared to the normal xerographic decay time, usually measured in seconds or minutes, the transit time is very small and hence the sweep-out of the mobile holes can be regarded as essentially instantaneous. Hence, after this process, the selenium layer and the upper part of the conducting substrate will have a total negative charge equal to the positive charge σ on the

selenium top surface, as illustrated in Fig.2.2. In practical xerographic situations, however, most of the negative charge will initially be in the substrate and very little in the selenium itself.

Fig.2.2

2.3 DARK DECAY PROCESS

With the positively charged plate left in the air under darkness, the potential at the surface can decrease with time due to three different $processes^{[1],[5]}$. These are:

(1) Neutralization of the charge arising from arrival of

electrons and negative ions on the free surface.

(2) Neutralization of the charge arising from injection of electrons from the conducting substrate into the selenium layer.

(3) The gradual release of holes from discrete centres located within the selenium layer.

Process (1) can be made to be very small, especially by the use of appropriate surface treatments. Process (2) is likely to be the most important process for pure undoped amorphous selenium and process (3) may be dominant for layers of chlorine-doped selenium, Se-Te alloys and As_2Se_3 .

2.4 TRAP-CONTROLLED INJECTION OF CARRIERS FROM SUBSTRATE

The flow of current from the conducting base is controlled by Schottky barrier action at the selenium-base interface or by trapping centres located at or near this interface. Since a relatively simple theory for the latter case has been developed by R. M. Schaffert^[5], this treatment only is reproduced here. Furthermore, Schaffert considered that dark decay cannot be explained by Schottky barriers alone.

Suppose the release of electrons from trapping centres control the electron current into the selenium from the substrate. It is supposed that after charging, a steady state is established, whereby the rate of filling of the traps is exactly balanced by their rate of emptying. If α is the probability of

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the release of an electron from one trap and N_f is the concentration of such traps, then the net release rate is:

$$\frac{dN_{f}}{dt} = -\alpha N_{f} , \text{ so that on integration}$$
$$N_{f} = N_{fo} e^{-\alpha t} ,$$

where N_{fo} is the initial concentration of filled traps, and since in the steady state

$$\frac{dn}{dt} = \frac{dN_{f}}{dt}$$

then

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 $\frac{dn}{dt} = -\alpha N_f = -\alpha N_{fo} e^{-\alpha t}$, which on integration dt

yields
$$n - n_0 = N_{fo} (e^{-\alpha t} - 1)$$

or $n = n_0 - N_{fo} (1 - e^{-\alpha t})$, (2.1)

where n_0 is the initial electron concentration.

The current i into the selenium is then given by:

$$i = \sigma E = ne\mu_n V/L$$
 (2.2)

if the electric field E is taken as uniform.

The capacitance per unit area of the selenium layer is $C=\epsilon_0\epsilon_r/L$, where ϵ_r is its relative dielectric constant and ϵ_0 is the permittivity of a vacuum. Since no current flows into the top surface from outside, the sum of the conduction and displacement currents must be zero. ie.

$$i + C \frac{dV}{dt} = 0$$

Hence

$$C \frac{dV}{dt} = -i \quad or \quad dV = -\frac{1}{C} i.dt$$

Substitution from equations (2.2) and (2.1) then yields:

$$\frac{dV}{V} = -\frac{e\mu_n}{\epsilon_0 \epsilon_r} n dt = -\frac{e\mu_n}{\epsilon_0 \epsilon_r} [n_0 - N_{fo} (1 - e^{-\alpha t})] dt$$

Integrating this, it becomes:

$$\ln\left(\frac{V_{o}}{V}\right) = -\frac{e\mu_{n}}{\epsilon_{o}\epsilon_{r}} \left[n_{o}t - \frac{N_{fo}}{\alpha}\left(e^{-\alpha t} - 1\right) - N_{fo}t\right]$$

where $V=V_0$ at t=0.

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This can be re-written:

$$V = V_0 \exp[-\frac{A_1}{\alpha} (1 - e^{-\alpha t}) - A_2 t]$$
, (2.3)

where
$$A_1 = \frac{N_{fo}e\mu_n}{\epsilon_o\epsilon_r}$$
 and $A_2 = \frac{e\mu_n}{\epsilon_o\epsilon_r} (n_o - N_{fo})$.

The type of decay of voltage with time, observed by Schaffert^[5] for xerographic plates with an approximate selenium thickness of 50 μ m, is shown in Fig.2.3. The solid lines, calculated with equation (2.3), using fixed values of A₁, A₂ and α , show a good fit to the experimental points.

2.5 DEPLETION DISCHARGE MODEL

If the interfacial film between the selenium layer and the conducting substrate effectively blocks carrier-injection from the base or if the photoreceptor material has bulk centres that are more easily ionized by thermal action (such as in Se-Te alloys), then process (3) can be dominant in describing the fall-off of voltage with time. In this process, the bulk density of negative charge (assuming again positive charging of the top surface) increases with time as the discrete centres progressively release holes into the valence band of the photoreceptor by thermal action. Each hole is quickly swept into the base, leaving behind an extra negatively charged centre. Assuming no loss of the surface charge σ with time, this charge is numerically equal to the total quantity of negative charge located within the receptor layer and in the conducting substrate. As the charge density within the receptor layer $\rho(z)$ increases with time, the space charge width within the layer eventually contracts and becomes less than the layer thickness L. As a result, the voltage across the photoreceptor layer is

progressively reduced.

This process has been treated by Abkowitz and Maitra^[6] and is described as follows (Fig.2.4). From Gauss's theorem, the electric



field E at a position z measured downwards from the receptor surface, assumed positively charged, is given by:

$$\epsilon_0 \epsilon_r E = \sigma - \int_0^z \rho(z) dz \qquad , \qquad (2.4)$$

where $\rho(z)$ is the bulk volume charge density at z.

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At z, the electrostatic potential is given by $-\int_{0}^{\infty} E. dz$. However, the voltage V is the potential at the receptor surface z=0 with respect to the ground base at z=L. Hence for V, the sign is changed to give:

$$V = \int_{0}^{z_{o}} E.dz , \qquad (2.5)$$

where z_0 is the value of z at which E is zero.

Substitution of equation (2.4) into equation (2.5) yields:

$$\mathbf{v} = \frac{1}{\epsilon_0 \epsilon_r} \left[\int_0^{z_0} \left\{ \sigma - \int_0^z \rho(z) dz \right\} dz \right] \qquad (2.6)$$

Within the receptor layer of thickness L, the charge per unit area $Q_{T_{i}}$ is:

$$Q_{L} = \int_{0}^{L} \rho(z) dz$$

Initially, Q_L is less than σ because most of the negative charge exists in the conducting base, so that $z_0=L$.

Eventually, as $\rho(z)$ grows with time, the space charge layer will extend just across L with no charge in the base. With further increase of $\rho(z)$, the space charge width will be less than L ie $z_0 \leq L$. In this case, $Q_L = \sigma$.

Suppose, for simplicity, that ρ is independent of z but that it still increases with time. In this case, equation (2.6) becomes:

$$V = \frac{1}{\epsilon_0 \epsilon_r} (\sigma z_0 - \frac{\rho z_0^2}{2}) \qquad (2.7)$$

Consider the initial time period, which may be denoted as zone 1, in which $Q_L < \sigma$. Since $Q_L = \rho L$ and $z_o = L$, equation (2.7) yields:

$$V = \frac{1}{\epsilon_0 \epsilon_r} (\sigma L - \frac{\rho L^2}{2}) = \frac{L}{\epsilon_0 \epsilon_r} (\sigma - \frac{\rho L}{2}) . \quad (2.8)$$

In the later time period, denoted as zone 2, $z_{o} \leq L$ and $Q_{L} = \sigma$, so that $\rho z_{o} = \sigma$. From equation (2.6), the voltage is now given by:

$$V = \frac{1}{\epsilon_0 \epsilon_r} (\sigma z_0 - \frac{\rho z_0^2}{2}) = \frac{\sigma^2}{2\epsilon_0 \epsilon_r \rho} \qquad (2.9)$$

Thus, as ρ increases with time t, the voltage falls according to equation (2.8) in time zone 1. When ρ reaches a value such that the negative space charge just spreads across the selenium layer at a time denoted by t_d , equation (2.9) starts to take over. For t>t_d, the charge depletion width gets to be less than L and the voltage falls according to equation (2.9).

In zone 1 for t<td, differentiation of equation (2.8) gives:

$$\left(\frac{dV}{dt}\right)_{i} = -\frac{L^{2}}{\epsilon_{0}\epsilon_{r}}\frac{d\rho}{dt} , \qquad (2.10)$$

assuming no loss of surface charge ie. $d\sigma/dt=0$.

In zone 2 for $t \ge t_d$, differentiation of equation (2.9) gives:

$$\left(\frac{dV}{dt}\right)_{2} = -\frac{\sigma^{2}}{2\epsilon_{0}\epsilon_{r}\rho^{2}}\frac{d\rho}{dt} \qquad (2.11)$$

It may be noted that at t=0, ρ can be taken as zero, so that from equation (2.8), the initial voltage V₀ is given by:

$$V_{o} = \frac{L\sigma}{\epsilon_{o}\epsilon_{r}} \qquad (2.12)$$

However, at t=t_d, from equation (2.9) and the fact that $\sigma=\rho L$, the voltage V_d is given by:

$$v_{d} = \frac{\sigma L}{2\epsilon_{0}\epsilon_{r}} \qquad (2.13)$$

Hence the present treatment predicts that $V_d/V_o=1/2$ ie. the voltage at t=t_d should be half the initial value.

Abkowitz and Maitra^[6] in their treatment assumed that the ionization of the discrete centres in the photoreceptor yields a bulk space charge density which increases with time according to the relation:

$$\rho(t) = at^p$$

where a and p are time-independent parameters.

Using this relation, equations (2.10) and (2.11) become

,

$$\left(\frac{dV}{dt}\right)_{i} = -\frac{L^{2}}{\epsilon_{0}\epsilon_{1}} \text{ apt}^{p-1} \text{ for } t < t_{d}$$
, (2.14)

and

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$$\left(\frac{\mathrm{d} v}{\mathrm{d} t}\right)_{2} = -\frac{\sigma^{2}}{2\epsilon_{0}\epsilon_{r}} \frac{\mathrm{apt}^{p-1}}{(\mathrm{at}^{p})^{2}} = -\frac{\sigma^{2}}{2\mathrm{a}\epsilon_{0}\epsilon_{r}} \mathrm{pt}^{-p-1} \qquad \text{for } t \ge t_{d} ,$$

which, with equation (2.12), namely $\sigma = V_0 \epsilon_0 \epsilon_r / L$, becomes:

$$\left(\frac{dV}{dt}\right)_{2} = -\frac{\epsilon_{0}\epsilon_{r}}{2a} \left(\frac{V_{0}}{L}\right)^{2} \text{ pt}^{-p-1} \qquad (2.15)$$

Thus, dV/dt changes abruptly at $t=t_d$ from a t^{p-1} dependence to a steeper negative slope with a dependence of the form t^{-1-p} . It is noted that the sum of the powers of t before and after t_d is -2. At $t=t_d$, since $\sigma=\rho L$, t_d is given by

$$t_{d} = \left(\frac{\rho}{a}\right)^{1/p} = \left(\frac{\sigma}{aL}\right)^{1/p} = \left(\frac{2V_{d}\epsilon_{o}\epsilon_{r}}{L^{2}}\right)^{1/p} , \quad (2.16)$$

using equation (2.13). Hence if p=1, for instance, t_d would be proportional to V_d .

Note also that if layers of different thickness L are charged to the same initial field V_0/L , then from equation (2.15) dV/dt for $t \ge t_d$ would be independent of L but for $t < t_d$, the voltage slope should be proportional to L^2 (equation (2.14)).

Fig.2.5 shows a plot of dV/dt against t on double logarithmic scales for Se-Te alloys measured by Abkowitz and Maitra^[6]. Here, the abrupt change of slope for the two alloys studied is clearly evident and hence, in this case, the depletion discharge process was dominant over injection from the base.



Fig.2.3 Theoretical and experimental dark decay curves for amorphous Se xerographic plates. Solid lines are culculated curves using eqn.2.3. Thickness of Se layers is approximately 50 μ m. (From Schaffert^[5].)



Fig.2.5 Log-log plot of dV/dt versus time t for samples prepared by Se-Te alloys initially charged to 100 V. Thickness of Se-Te layers is 55 μ m. (From Abkowitz and Maitra^[6].)

CHAPTER 3 TECHNIQUES OF SAMPLE PREPARATION

3.1 INTRODUCTION

In the present work the samples for study were essentially of the same form, consisting of an aluminum substrate, a thin film of aluminum oxide, usually a few hundred angstroms in thickness and a layer of evaporated selenium usually with a thickness of some tens of micrometers. Some 110 samples of this form were made for xerographic measurements and Table 3.1 summarizes the fabrication details of them. For the investigation of the intermediate oxide layer, many samples were also prepared consisting of just the aluminum plate plus the oxide layer with small deposited areas of Wood's metal but without the selenium layer. These were used for measurements of capacitance and resistance of the oxide. The present chapter describes in detail the processes employed to prepare the samples used for the measurements reported in chapters 5 and 6.

3.2 SUBSTRATE CLEANING AND ETCHING

A plate of aluminum 0.035 inch in thickness and 2 X 2 inches in lateral dimensions was used as the base electrode and substrate for the selenium films. The aluminum plates, which were polished on one surface to a mirror finish, were kindly supplied by the Noranda Technology Centre in Pointe Claire. After cutting each sheet into the sample size given, the plate was ultrasonically cleaned by immersion for 10 minutes each in ethyl alcohol, acetone and deionized water. It was then dried in air or nitrogen. An etching treatment was then applied to remove the naturally formed oxide film because of its poor quality^[15]. The etching also served to remove any surface contamination. Two different processes were used for the etching step (see Table 3.1, footnote 1). In one (etch a), the aluminum plate was etched in chromic/phosphoric acid (20 g CrO₃ plus 35 ml 85% H₃PO₄ per liter) at 90°C for 10 minutes. In the other (etch b), the plate was etched in sodium carbonate/sodium orthophosphate (25 g Na₂CO₃ plus 162 g Na₃PO₄.12H₂O per liter) at 65°C for 1.5 minutes, followed by further etching in HNO3 for 1 minute. After etching, the specific oxidation process was immediately employed to avoid possible contamination.

3.3 FORMATION OF INTERMEDIATE OXIDE FILM BY THERMAL OXIDATION

A thin aluminum oxide film was next formed on the etched surface of the aluminum substrate. Several different methods were used for this but only one, the thermal method will be described now, as this was the method mostly employed for the oxidation process. The other methods will be described in section 3.6.

The etched aluminum substrate was placed on a flat plate of fused quartz, which was inserted into the open tube of a Lindberg Hevi-duty (model 54357A) furnace. The furnace was then switched on and the temperature of the sample was raised to a constant value, which was maintained for 2 hours. The temperature used for each sample is given in column 3 of Table 3.1 but usually the temperature was 400°C. After the heating period, the furnace was switched off, allowing the sample to cool down slowly to avoid substrate deformation.

3.4 SELENIUM DEPOSITION

The aluminum substrate, coated with its thin oxide film, was next mounted in a graphite holder inside the Bell jar of a 12inch vacuum coater (Edwards model E12E) and positioned about 10 cm above the selenium source. The graphite holder was heated by

two 75 Watt heating elements and controlled by a temperature controller (Omega) with a type J thermocouple inserted in the graphite. The schematic arrangement for selenium evaporation, with a rotatable shutter in front of the substrate, is shown in Fig.3.1. In the course of this study, two different evaporating source boats were used (Fig.3.2 (a) and (b)). Samples Z-1 to Z-29 were evaporated with a tantalum boat, while samples after Z30 were evaporated from a stainless steel crucible. With either source, the chamber was first cleaned with a vacuum suction cleaner and then with isopropyl alcohol to remove possible contaminants before each evaporation run.

The boat was loaded with selenium pellets and the system was pumped down to a pressure of 10^{-6} Torr. Then, with the shutter in front of the substrate, the temperature of the substrate was raised to the desired temperature (30 to 80° C in this study) and stabilized at this point for 30 minutes. Next the source heater was switched on and, at a suitable time, the shutter was opened to allow deposition of the evaporating selenium on to the substrate. After sufficient selenium had been deposited, the shutter was closed and the source heater switched off. The substrate was allowed to cool in its evaporation position for about two hours before removal from the vacuum system. Following this, a small piece of the deposited selenium layer was chipped off and used for thickness measurement by setting it on its edge under an optical microscope.

The evaporation procedures were a little different in using the two types of boats, as explained as follows.

Tantalum boat

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For the first 29 samples, the evaporation boat was made from tantalum sheet (see Fig.3.2(a)). This was very convenient in that large quantities of selenium pellets could be evaporated when needed. However, no thermocouple could be easily used with this type of boat, so that there was no control of source temperature. During the evaporation, which was usually 10 to 16 minutes, the current through the boat was 2.5 to 3 amps.

Stainless steel crucible

For all evaporation runs beyond sample Z-29, ie. for samples Z-30 to Z-110, the selenium was evaporated from a stainless steel crucible. This is shown schematically in Fig.3.2(b). It consisted of a stainless steel cup located in a crucible of fused quartz, which was itself supported in a basket of tungsten wire, through which the current was passed. A type J thermocouple, located in a hole in the stainless steel cup, served to measure its temperature. In the evaporation, the source temperature was increased to 200°C and maintained at this value for 15 minutes, with the shutter still in front of the substrate, in order to enable dissolved gas in the selenium to be released. The evaporation time between opening and closing of the shutter was usually about an hour with this crucible.

3.5 WOOD'S ALLOY DEPOSITION

In this study, many oxidized samples were prepared in pairs under the same conditions to ensure consistency; one sample was used for xerographic measurements, after coating with amorphous selenium film, while the other, without selenium, was employed for capacitance and resistance measurements and used to determine the thickness of the oxide films and to assess their quality. The upper electrodes for these latter samples were obtained by evaporating small areas of Wood's metal through a metal mask on top of the oxide.

Wood's metal is an alloy made up of 50% bismuth, 25% lead, 12.5% tin and 12.5% cadmium, having a melting point of 71°C. It was used because of its low melting point and hence lower risk of damaging the thin oxide film during evaporation. A metal mask (Fig.3.3), located in front of the oxide on the aluminum substrate, was used to define the deposited areas of Wood's alloy (from 0.008 to 0.26 cm²). For the evaporation of the Wood's metal, the sample, with its mask, was located in a 6-inch bell jar (Edwards model 6E4) vacuum system, and positioned about 8 cm above a molybdenum boat containing Wood's metal. The chamber was then pumped down to a pressure well below 10^{-4} Torr, and the Wood's metal was evaporated for 5 minutes at a current of about 35 A through the boat. After evaporation was completed, the sample was allowed to cool down for 30 minutes and then removed for capacitance and resistance measurements.

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3.6 OTHER METHODS OF FORMATION OF INTERMEDIATE OXIDE FILM

In section 3.3, one method was described for forming the aluminum oxide film between the selenium and the aluminum substrate. In fact, many methods were used in the present work and the results obtained with them are reported in chapter 6. The other methods are now described.

(a) D.C. Reactive Sputtering

A convenient method of obtaining oxide films with thicknesses in the range from a few hundred to several thousand angstroms is d.c reactive sputtering. In this, the sputtering takes place from an aluminum target in the presence of oxygen. The process can be controlled via the sputtering power, the gas pressure and composition and the anode-to-cathode separation^{[16][17]}.

The arrangement used for forming the oxide film in this study is shown in Fig.3.4, utilizing a 12 inch Edwards model E306A coating system. The target consisted of an aluminum plate 3 mm in thickness and 50 mm in diameter, which was coated with several micrometers of pure aluminum (99.999%) by evaporation. With this plate mounted at the cathode, the aluminum substrate to be oxidized was placed at the anode with a target-substrate separation of 40 mm. The chamber was pumped down to an initial pressure of 10^{-5} Torr and the high vacuum valve was shifted to the "glow discharge" position, Next, the gas was introduced via the inlet needle valve and the chamber pressure was set to an

appropriate value by careful adjustment of the high vacuum value and the inlet needle value. Three different gas compositions were used in the reactive sputtering: air, 95%Ar+5%O₂ and 50%Ar+50%O₂. The chamber pressures for sputtering to obtain a dark space of about a third to a quarter of the target-substrate separation were respectively 80, 40 and 100 mTorr for the three gas compositions. To obtain a sputtering current of 40 mA, the d.c. voltages were 1.2, 2 and 1 kV respectively for the air, 5%O₂ and 50%O₂ gas compositions. The sputtering was carried out in successive 15 minute periods with 30 to 60 minutes between each to prevent overheating of the target. The total sputtering time varied from 3 minutes to 6 hours.

(b) Thermal Oxidation

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Besides the thermal oxidation in air described in section 3.3, two other variations were tried.

(i) Aluminum substrate heated in oxygen under reduced pressure

In this method the sample was heated under reduced pressure inside a 12 inch Edwards model E12E3 vacuum system for 2 hours. The sample was mounted on a stainless steel holder, which was attached to a heating plate (Chromalox WS-605). A thermocouple, inserted in a small hole in the sample holder, served to measure and control the temperature during heating via a temperature controller feeding current to the heater. The system was first pumped down to a pressure of about 10^{-6} Torr and the temperature raised gradually to degas the substrate by adjustment of the

temperature controller. After about an hour, the temperature was adjusted to the desired value in the range 50°C to 300°C and the high vacuum valve was closed. Then pure oxygen gas was allowed into the chamber via the inlet needle valve and the pressure was adjusted to be 10 mTorr by partial opening of the high vacuum valve. The sample was maintained at the set temperature and pressure for 2 hours, following which the heater current was switched off and the sample allowed to cool to room temperature before removal from the system.

(ii) Heating in oxygen after degassing under vacuum

The oxidation in this process was carried out in pure oxygen under atmospheric pressure after the sample had been degassed by heating under vacuum. The procedure during vacuum heating was the same as that in (i) above, except that a different vacuum system was used (Edwards model E306A).The heating at a pressure of 10^{-6} Torr was at a temperature of 200°C for an hour. Following this, the chamber was allowed to reach atmospheric pressure and the heating at 200°C was maintained for the designated time.

(c) A.C. Glow Discharge

Oxidation of the aluminum was done in an a.c. glow discharge in the presence of argon plus a trace of residual air. In this method, the aluminum substrate was first placed on the grounded metal shutter inside an Edwards model E306A vacuum system containing its "Plasmaglo accessory". This accessory is shown schematically in Fig.3.5 and consists of two metal rings supplied with voltage at the mains frequency of 60 hertz. It incorporates

a cylindrical metal shield inside the rings and the sample was positioned in the centre of the space within this cylinder. The chamber was first pumped down to a pre-pressure of 7.5 mTorr. Then, with the high vacuum valve set to the "glow discharge" position, the gas inlet valve was set to 50 units (arbitrary scale) to allow high purity argon to flow through the chamber under a gas bottle pressure of 5 psi. Next the chamber pressure was raised to 50 to 100 mTorr and an a.c. voltage of 2 kV (RMS) was applied between the ring electrodes to produce a plasma for 10 minutes. After this period, air was let into the chamber and the sample was allowed to cool at atmospheric pressure for 10 minutes. Following this, the system was pumped down again to 7.5 mTorr and the process repeated. This was repeated for several cycles for the total exidation period required. The process resulted in a thin oxide film from the reaction of the aluminum with oxygen remaining in the system from the step with 7.5 mTorr air pre-pressure.

(d) D.C. Glow Discharge with Sample at Cathode

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In the case of reactive sputtering, described above (a), the sample was placed at the anode. However, some oxidation also occurs at the cathode and therefore some experiments were carried out to see if this could be used for oxide formation. Accordingly, with an Edwards vacuum system (model E306A), the sample was located at the cathode position separated by 40 mm from a plate of aluminum acting as the anode. The chamber was pumped down to an initial pressure of about 10^{-4} Torr and the high vacuum valve was set to the "glow discharge" position. Air was allowed to flow
through the chamber at a stable pressure of 30 mTorr by adjustment of the inlet needle valve and the high vacuum valve. Then, a d.c. voltage of 2kV was applied between the electrodes to produce the glow discharge for the period required of 30 to 120 minutes. It was apparent that while a thin oxide film was produced by this process, etching of the aluminum substrate at the cathode also took place by the sputtering action of the bombarding ions.

(e) D.C. Glow Discharge

Oxidation was also carried out with the same arrangement as in reactive sputtering, described above (a), but with a greater electrode separation (80 mm) and a small d.c. voltage (800 volts) to maintaining sputtering. Thus the cathode-to-anode distance was twice and the voltage two thirds of the value for air used in (a). The system was first pumped down to a pressure of 10^{-4} Torr and with the high vacuum valve set to "glow discharge", air was allowed to flow through the chamber via the inlet needle valve. With the pressure adjusted to 100 mTorr the voltage was applied to the electrodes to produce the glow discharge, which was maintained for 15 minutes. As will be reported in chapter 6, tests with glass substrates at the anode showed that negligible sputtering of the aluminum took place from the cathode to the anode under the conditions employed.

Table 3.1 Details of Fabrication of Selenium Film Samples

	Al Substrate			Se Deposition				
Sam ple No.	Sur- ¹ face treat ment	2 Oxidation Methods	Oxide ³ Thick- ness (Å)	Subst. Temp. (°C)	Source Temp. (°C)	4 Type of boat	Se Film ⁵ Thick- ness (µm)	Remarks
Z001 Z002 Z003 Z004 Z005 Z006 Z007 Z008 Z009 Z010 Z011 Z012 Z013 Z014 Z015 Z016 Z017 Z018 Z019 Z020 Z021 Z022 Z023 Z024 Z025 Z026 Z027 Z028 Z029 Z020 Z021 Z022 Z023 Z024 Z025 Z026 Z027 Z028 Z029 Z030 Z031 Z032 Z033 Z034 Z035 Z036 Z037 Z038 Z039 Z040	aaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaa	A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.200°C A.200°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C A.400°C	180 180 180 180 180 180 180 180	50 50 50 50 50 50 50 50 50 50 50 50 50 5	- - - - - - - - - - - - - - - - - - -	ŢŦŦŦŦŦŦŦŦŦŦŦŦŦŦŦŦŦŦŦŦŦŦŦŦŦŦŦŦŦŦŦŦŦŦŦŦŦ	50 50 50 50 50 50 50 50 50 50 50 50 50 5	peeled

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Table 3.1 (continued) Details of Fabrication of Selenium Film Samples

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	Al Substrate			Se Deposition				
Sam ple No.	Sur ¹ face treat ment	2 Oxidation Methods	Oxide ³ Thick- ness (Å)	Subst. Temp. (°C)	Source Temp. (°C)	4 Type of boat	Se Film ⁵ Thick- ness (µm)	Remarks
No. Z041 Z042 Z043 Z044 Z045 Z046 Z047 Z048 Z049 Z050 Z051 Z052 Z053 Z054 Z055 Z056 Z057 Z058 Z059 Z060 Z061 Z062 Z063 Z064 Z065 Z066 Z067 Z068 Z069 Z070 Z071 Z072 Z073 Z074 Z075 Z076 Z077 Z078 Z079	ment aaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaa	Methods C. 2hrs. C. 1hr. C. 30min. A. 400°C A. 400°	 (Å) 120 90 50 180 <	(°C) 50 50 50 50 50 50 50 50 50 50	(°C) 245 245 245 245 260 270 280 260 260 260 260 260 260 260 26	boat SSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSS	(μm) 55 40 40 45 45 42 50 45 48 20 10 42 50 68 80 55 55 45 - 40 40 40 40 40 40 40 40 40 40 40 60 58 58 60 65 65 65 65 65 65 65 65 65 65 65 65 65	peeled

Table 3.1 (continued) Details of Fabrication of Selenium Film Samples

	Al Substrate			Se Deposition				
	Sur-1	2	$Oxide^3$			4	Se Film ⁵	
Sam	face		Thick-	Subst.	Source	Type	Thick-	Remarks
ple	treat	Oxidation	ness	Temp.	Temp.	of	ness	
No.	ment	Methods	(Å)	(°C)	(°C)	boat	(µm)	
Z081	a	G.1hr.	1290	50	255	S	60	
Z082	a	G.6hrs.	3000	50	255	S	60	
Z083	a	G.30min.	880	50	255	S	60	
Z084	a	H.1hr.	1400	50	255	S	65	
Z085	а	H.3min.	320	50	255	S	65	
Z086	a	H.15min.	500	50	255	S	60	
Z087	а	H.30min.	880	50	255	S	60	
Z088	a	H.lhr.	1400	50	255	S	62	
Z089	a	H.3hrs.	2310	50	255	S	60	
Z090	a	H.6hrs.	3180	50	255	S	60	
Z091	a	G.3min.	240	50	255	S	60	
Z092	a	F.3min.	280	50	255	S	62	
Z093	a	E.30min.	90	50	255	S	60	
Z094	a	E.4hrs.	190	50	255	S	65	
Z095	a	E.3hrs.	180	50	255	S	60	
Z096	a	E.2hrs.	160	50	255	S	65	
Z097	а	E.1hr.	130	50	255	S	65	
Z098	a	E.30min.	90	50	255	S	65	
Z099	a	E.15min.	60	50	255	S	65	
Z100	b	J	-	50	255	S	60	
Z101	b	E.1hr.	130	50	255	S	60	
Z102	b	I.15min.	240	50	255	S	60	
Z103	b	I.15min.	-	50	255	S	60	V=1.7kV
Z104	a	E.1hr.	130	50	255	S	60	
Z105	а	J	-	50	255	S	65	
Z106	а	I.15min.	240	50	255	S	60	
Z107	a	J	-	50	255	S	60	
Z108	a	I.15min.	240	50	255	S	60	
Z109	b	J	-	50	255	S	58	
Z110	b	I.15min.	240	50	255	S	58	

1/ Surface treatment:

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Each aluminum substrate was cleaned ultrasonically by immersion for 10 minutes each in ethyl alcohol and acetone. This was then treated by one of the following:

- a: etching in chromic/phosphoric acid at 90°C for 10 minutes; or
- b: etching in sodium carbonate/sodium orthophosphate

 - at 65°C for 1.5 minutes, then etched in HNO3 for 1 minute.

2/ Methods of oxidation were as follows: A: air heating for 2 hours, temperature as indicated; B: vacuum heating for 2 hours, temperature as indicated;

- C: A.C. glow discharge for the times indicated;
- D: cathodic sputtering for the times indicated;
- E: degassing and heating at 200°C in pure oxygen for the times indicated;
- F: reactive sputtering with 5%0₂+95%Ar, for the times indicated; G: reactive sputtering with air, for the times indicated;
- H: reactive sputtering with 50%02+50%Ar, for the times indicated;
- I: D.C. glow discharge for the times indicated;
- J: no oxidation.
- 3/ Thicknesses measured by capacitance.
- 4/ Selenium was evaporated either from a boat of tantalum (T) or stainless steel (S).
- 5/ Thicknesses measured with optical microscope.



Fig. 3. 1 Schematic of vacuum system for selenium evaporation





Fig.3.2 Schematic diagrams of (a) the tantalum boat and (b) the stainless steel crucible used for the selenium evaporation.

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Fig.3.3

Aluminum mask for Wood's alloy electrode evaporation.





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Fig.3.5 Schematic diagram of "Plasmaglo" accessory for a.c. glow discharge. (From Edwards operating manual)

CHAPTER 4 MEASUREMENT TECHNIQUES

4.1 INTRODUCTION

The methods of measurement made to characterize the xerographic electrical and optical behavior of the deposited amorphous selenium films after fabrication are described in this chapter.

These measurements were:

(1) Surface potential of the selenium film after charging in darkness as a function of time and after illumination.

(2) Aluminum oxide thickness measurement by capacitance and interference methods.

(3) Selenium film thickness measurement.

4.2 POTENTIAL MEASUREMENT

In order to analyse the electrophotographic properties of the selenium film samples, the surface potential variation after

charging was measured. A simple, practical apparatus was therefore set up for this, which yielded satisfactory results. This is now described.

(a) Complete Measuring Apparatus

Fig.4.1 shows an overall diagrammatic view of the apparatus used for measuring the xerographic properties. The main part of the apparatus consisted of an aluminum rotatable disk, over which was positioned a fixed aluminum table, whose surface was parallel to the disk. A brass holder was mounted on the turntable to support the selenium sample deposited on its aluminum substrate. The fixed table carried a corotron charging unit, the probe for measuring the electrostatic potential and a lamp for illuminating the sample. By locating the selenium sample under the corotron unit, the sample could be charged. Then by rapid rotation, the sample could be brought under the measuring probe for potential determination. With the film in this position, the surface potential of the selenium film could be followed with time. Then after a fixed time, the disk was rotated so that the sample was located underneath the illumination source to discharge the Se plate. By rotating the disk back to the position where the sample was under the measuring probe, the residual potential could be measured.

(b) Corotron Charging Device

A most effective and reliable method of electrically charging a xerographic photoreceptor is by spraying the plate surface with ions produced by a corona discharge. When a

potential of several thousand volts is maintained between a grounded shield and a fine wire, corona emission from the wire ionizes air molecules, which are drawn to the photoreceptor surface, thus charging it. Such a device is known as a corotron.

A simple corotron was constructed in the laboratory (Fig.4.2). It consisted of a U-shaped cylindrical shield made from aluminum-alloy sheet. The charging wire consisted of a single strand of 0.1 mm diameter copper wire, fixed between two rods of brass mounted on a Teflon block. The entire corotron device was then mounted on the fixed table as indicated in Fig.4.1.

The shield of the corotron was connected to ground and during charging the voltage on the wire was maintained for few minutes at about 6500 volts from a Sorenson model 1202-30 high voltage supply. The selenium plate could be charged either positively or negatively with respect to ground by reversing the polarity of the power supply.

This charging device worked very satisfactorily and was able to charge the xerographic film surface up to 800 volts under dark conditions.

c) Electrometer

The electrometer used for the potential measurements was a model 610C Keithley electrometer with an input resistance of 10^{14} ohm and an input capacitance (with the connecting coaxial cable) of 20pF. As indicated in section 4.2(d) below, the charge

leakage rate in this instrument was sufficiently low for the present measurements. The potential variations were recorded on the time base of a Hewlett Packard model 7015B X-Y pen recorder. The response time of the measuring system to potential changes was found to be less than 0.3 second. It was also found to be important to use Teflon as the insulator in the measuring probe because of its high bulk resistivity, low affinity for surface contamination and ease of fabrication. This same material was also used in the connecting coaxial cable. Initially Plexiglass was used and the charge leakage rate was found to be unacceptably large for measuring the true decay rates associated with the selenium film under study.

(d) Plate Potential Determination

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The electrostatic potential on the charged selenium film was determined by measuring the potential (V_m) on a small circular measuring plate (diameter 15 mm) of copper positioned parallel to the film but at a fixed distance from it of usually 2mm. The actual potential of the charged surface of the selenium film (V_p) can be found from V_m if the following capacitances are known:

(1) the capacitance C_p between the top surface of the selenium film and aluminum substrate

(2) the capacitance C_e between the measuring plate and the selenium surface

(3) the capacitance C_m of the measuring electrometer and the associated leads.

(i) Measured Potential

Fig.4.3(a) shows schematically the charged plate and equivalent circuit. Fig.4.3(b) shows the measuring arrangement and Fig.4.3(c) shows the equivalent circuit of the complete measuring arrangement.

The capacitances C_e and C_p are given respectively by the relations:

$$C_e = \frac{\epsilon_o A_e}{d_e}$$
 and $C_p = \frac{\epsilon_{rse} \epsilon_o A_p}{d_p}$,

where

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 ϵ_{o} is the permittivity of a vacuum = 8.84x10⁻¹⁴ F/cm

 $\epsilon_{
m rse}$ is the relative dielectric constant of amorphous selenium, taken as 6.4

d_e is the separation between the measuring plate and the selenium film top surface

 d_p is the thickness of the selenium film A_e is the area of the measuring plate A_p is the area of the selenium film .

From Fig.4.3(c) it is seen that C_m and C_e form a capacitance voltage divider across C_p , so that the measured potential V_m is given by:

$$V_{\rm m} = V_{\rm pf} \frac{1/C_{\rm m}}{1/C_{\rm e}+1/C_{\rm m}} = \frac{C_{\rm e}}{C_{\rm e}+C_{\rm m}} V_{\rm pf}$$
 (1)

where V_{pf} is the "final" potential of the charged selenium top surface (with respect to the grounded substrate) when the

measuring plate is located above the film. With the selenium film not under the measuring plate, the potential of the top selenium surface is simply given by

$$v_p = \frac{Q}{c_p}$$
 . $c_p \prod_{i=1}^{n} v_p$

Hence, with the film under the measuring plate, the charge Q has to be shared also with the capacitor arising from C_e and C_m in series so that

$$Q = Q_1 + Q_2$$

where Q_1 and Q_2 are the charges on the selenium plate and measuring plate respectively.



$$c_p v_p = c_p v_{pf} + v_{pf} \frac{c_e c_m}{c_e + c_m}$$

yielding

Hence

$$v_{p} = v_{pf} \{ 1 + \frac{c_{e}c_{m}}{c_{p} (c_{e} + c_{m})} \}$$

so that

$$V_{pf} = V_p \frac{C_p (C_e + C_m)}{C_e C_p + C_p C_m + C_e C_m}$$
 (2)

Hence, from equation (1),

$$v_{\rm m} = v_{\rm p} \frac{c_{\rm e}c_{\rm p}}{c_{\rm e}c_{\rm m} + c_{\rm p}c_{\rm m} + c_{\rm e}c_{\rm m}}$$
 (3)

In the present experiments the following capacitance values were measured:

 $C_{\rm p} = 2.78 {\rm nF}$ $C_{\rm e} = 0.78 {\rm pF}$ $C_{\rm m} = 20 {\rm pF}$.

Therefore from equation (2),

$$V_{pf} = 0.9997 V_{p}$$
,

so that V_{pf} can be taken without serious error to be V_p Hence from equation (1),

$$v_{m} = v_{pf} \frac{c_{e}}{c_{e} + c_{m}} = 0.0375 v_{pf} = 0.0375 v_{p}$$

That is

$$v_{\rm p} = \frac{v_{\rm m}}{0.0375} = 26.7 v_{\rm m}$$

Thus, the actual potentials on the selenium surface were obtained by multiplying the voltage on the measuring plate, determined by the electrometer, by a factor of 26.7. Fig.4.4 shows the actual measured potential V_m on a selenium film as a function of time.

(ii) Charge Leakage Rate of Measuring System

It is important that the leakage rate for charge on the electrometer should be smaller than the leakage rate of charge from the selenium film itself. The decay time τ for the electrometer connected to the measuring plate is given by the instrumental input resistance R_m multiplied by the capacitance seen at the input terminal. Thus



With this estimated decay time for the instrument of some 30 minutes, the measurements of decay time of charge on the selenium films were considered to be sufficiently accurate, since the time period for such measurements was arranged to be only 2 minutes. However, to confirm the instrument decay time, a selenium film was charged and the measuring probe positioned over the film. Then the film sample was rotated away from the measuring probe. With the probe connected to just the electrometer via the special co-axial cable, the voltage was recorded as a function of time for 4 minutes. In this time, the voltage decay amounted to less than 2%. This corresponds to a decay time of some 3 hours.

(e) Potential Measurement Procedure

The procedure for characterizing the charging and illumina-

tion of the xerographic selenium plate in this study was as follows:

1. The sample was mounted in the brass sample holder on the rotatable aluminum plate, which was then rotated to bring the sample underneath the corotron. The selenium surface was then charged by switching on the d.c. power supply set at 6.5 kV and the sample was then oscillated back and forth underneath the corotron wire to insure uniform charging for a few seconds.

2. The charged selenium plate was rotated to the fixed position underneath the potential measuring plate and the potential was then measured with the connected electrometer and recorded as a function of time.

3. After two minutes under dark conditions, the sample was rotated under a tungsten exposure lamp (8 watt), which was switched on to illuminate the sample for 5 seconds.

4. The selenium sample, with its residual charge, was then rotated until it was re-positioned underneath the potential measuring probe and the residual potential was measured and recorded.

From the trace on the recorder chart paper (such as that shown schematically in Fig.4.5), the characteristics of the film were determined according to the following definitions:

The Acceptance Potential (v_A) was taken as the maximum potential in darkness following the charging. It represents the voltage at which the charge leaks away at the same rate as it is supplied.

The Residual Potential (V_R) was taken as the potential measured 5 seconds after the switching on of the illumination.

The Dark Decay Rate (%) was taken as the ratio $(\mathbf{v_A} - \mathbf{v_2}) / \mathbf{v_A}$, where $\mathbf{v_A}$ is the acceptance potential defined above and $\mathbf{v_2}$ is the dark potential taken 2 minutes after the initial charging.

The Voltage Contrast was taken as the ratio V_2/V_R where V_2 and V_R are as defined above.

The other characteristics involved in the xerographic performance of the photoreceptor are cycled residual voltage and light fatigue. However tests of these characteristics were not made in the present studies.

4.3 ALUMINUM OXIDE THICKNESS MEASUREMENT

An aluminum oxide layer is usually employed between the selenium film and the aluminum substrate to reduce charge loss from the selenium film. It is helpful to know the thickness of the aluminum oxide layer and this was determined by capacitance and, where possible, also by interference. The thicknesses of the films obtained by vacuum methods described in chapter 3, ranged 60 to 4000 Å. The capacitance and interference methods are now described.

(a) Capacitance Method

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To measure the oxide thickness by this method, small areas of Wood's metal were evaporated on top of the oxide on the aluminum substrate, as described in chapter 3. Then the sample was

located in the pressure contact unit shown in Fig.4.6. Here each Wood's metal area was placed under a spring-loaded copper point with a small separate piece of Wood's metal between the point and the deposited metal to ensure contact over a sufficiently large area and to avoid damage to the oxide film. The back of the aluminum test plate, containing the selenium and aluminum oxide films, was in direct contact with the brass base plate of the test unit. Using the shortest possible leads, to minimize inductance, connection was made to the terminals of a Hewlett-Packard model HP4192 LF Impedance Analyzer .

The parallel capacitances and resistances were read directly from the displayed values on the instrument but, because of drift, it was found necessary to wait for periods of minutes to allow the readings to reach steady values. The values were measured with a signal level of $\triangle V = 0.1$ volt over the frequency range 100 Hz to 10 MHz.

Since the Wood's metal-oxide-Al capacitors were of the parallel plate type, the capacitance is given by:

$$C = \frac{\epsilon_0 \epsilon_{rox}^A}{d_{ox}}$$

where

 $\epsilon_{\rm rox}$ is the relative dielectric constant of aluminum oxide taken as 9,

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A is the area of the capacitor,

and d_{ox} is the thickness of aluminum oxide.

Since a plot of C against A would be a straight line, the oxide thickness can be determined from its slope (Fig.4.7).

(b) Interference Method

In the case of thicker aluminum oxide films, the thickness could also be determined by interference. Such films were prepared by reactive sputtering (see chapter 3), where it was possible to create a step in the oxide by screening off part of the substrate. Observation of this step under a microscope clearly revealed the colored interference fringes. From the final color of wavelength λ and its diffraction order N, the thickness d_{ox} of the oxide was determined using the relation:

 $2nd_{OX} = N\lambda$

where n is the refractive index of Al_2O_3 , taken as 1.67 ,

It was found helpful in this work to evaporate a very thin transparent aluminum film on top of the oxide film to enhance the reflectance of the top surface compared to the underlying surface of the aluminum substrate. This procedure was found ' increase greatly the visibility of the interference colors, not only on the steps, but on the overall surface as well.

Since in this method, the film must contain at least the distance $\lambda/2n$, it could only be used for thicknesses of more than about 1000Å. Fig.4.8 shows a plot of the thicknesses measured capacitatively against values measured by interference. It is noted that the agreement is surprising good, considering the uncertainty of the values of ϵ_r and n employed for the oxide film, which were assumed to be the bulk values.

4.4 SELENIUM FILM THICKNESS MEASUREMENT

The selenium film thicknesses were measured by chipping off a small piece of the selenium film from the edge of a sample. This piece was then erected on its edge and supported with a little grease on a microscope slide. It was then placed under an optical microscope and the thickness of the selenium film was determined by comparison with a microscope standard length scale. The error of the measurement by this method is considered to be less than 2.5μ m.



Fig. 4.1 Diagram of apparatus for measuring the xerographic properties



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Fig. 4.2 Corotron charging arrangement

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b. Measuring arrangment



c. Equivalent circuit of measuring arrangement

Fig. 4.3 Potential measurement scheme



Fig. 4.4

Variation of electrostatic potential with time as measured (solid line) directly on a typical selenium plate



Fig. 4.5

Definitions of the xerographic characteristics



Fig. 4.6

Pressure contact device used in capacitance measurement

Fig. 4.7

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Plot of capacitance against wood's metal contact areas for two different thicknesses of aluminium oxide

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Fig. 4.8 Plot of oxide thicknesses measured capacitively against values measured by interference

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CHAPTER 5 EFFECT OF SELENIUM DEPOSITION CONDITIONS

5.1 INTRODUCTION

The xerographic properties of amorphous selenium films are affected by the conditions of vacuum deposition and, in particular, by the film thickness, the temperature at which the selenium is deposited, the deposition rate and the concentration of chlorine in the selenium. Thus, in the present chapter the influence of these factors is examined. The experiments consisted of preparing samples with variation of one factor at a time and then measuring in them the parameters: acceptance voltage, residual voltage, dark decay rate and voltage contrast, as defined in chapter 4. In this study, the aluminum substrates were given the same oxidation treatment prior to selenium deposition, consisting of thermal oxidation at 400°C for 2 hours in air. The resultant oxide film was about 180 Å thick and acted as an interfacial barrier to limit carrier injection into the selenium from the aluminum base.

5.2 EFFECT OF SELENIUM FILM THICKNESS

To determine the effects of varying the selenium film thickness, six samples were prepared with thicknesses ranging from 10 to 80 micrometers. Table 5.1 shows details of these samples prepared at the same selenium deposition temperature of 50°C and with the same source temperature of 260 °C. The different selenium film thicknesses were obtained by increasing the weight of the selenium pellets in the evaporation boat and also by increasing the deposition time.

Figs.5.1 and 5.2 show the residual voltage V_R and acceptance voltage V_A plotted against selenium thickness for positive and negative charging respectively. It is seen that both V_R and V_A increase with increase of selenium film thickness for both charging polarities. However, for positive charging, the magnitudes of V_R and V_A are larger than the corresponding values for negative charging.

Dark decay rate and voltage contrast are plotted against selenium film thickness in Figs.5.3 and 5.4. For both charging polarities, these quantities decreased with selenium film thickness. It is also apparent that the magnitude of the decay rate was greater for positive than negative charging.

5.3 EFFECT OF SELENIUM DEPOSITION TEMPERATURE

To determine the effect of varying the substrate temperature during the selenium evaporation, six samples were deposited at different selenium substrate temperatures from 30 to 80 °C, keeping the source temperature constant at 260°C. Details are given in Table 5.2. Efforts were made to keep the selenium film thickness constant but this was not easy to control in the fabrication process. However, the thickness values were kept within a 20% range, as seen in the table (45 to 55 micrometers). An attempt to prepare a sample at a substrate temperature of 80 °C (not shown) resulted in the selenium film peeling off.

Figs.5.5 and 5.6 show plots of V_R and V_A against selenium deposition temperature for both charging polarities respectively. In the case of positive charging, it is noted that V_R decreased rapidly with deposition temperature, while V_A showed a tendency to increase. However, for negative charging, a maximum in both V_R and V_A occurred around 50 °C.

The dark decay rate and voltage contrast variations with deposition temperature are shown in Figs.5.7 and 5.8 for positive and negative charging respectively. It is seen that the decay rate showed a minimum in a temperature range of 40 to 50 °C for both positive and negative charging. The voltage contrast, on the other hand, increased with increase of substrate temperature for positive charging but showed a less definite trend with negative charging.

5.4 EFFECT OF SELENIUM DEPOSITION RATE

Six samples were fabricated with different deposition rates, ranging from 0.56 to 3.20 μ m/min, obtained by varying the source temperature and keeping the substrate temperature at 50 °C. The details are given in Table 5.3, where it is noted that the selenium film thicknesses ranged from 42 to 50 micrometers. As with the samples studied in sections 5.2 and 5.3, the oxidation of the aluminum plate was done thermally at 400 °C for 2 hours.

Plots of v_R and v_A against selenium deposition rate are given in Figs.5.9 and 5.10 for positive and negative charging respectively. It is seen that v_A did not vary much with deposition rate for both polarities but the magnitude of v_A was larger for positive than negative charging. It is also noted that v_R increased with deposition rate for positive charging but showed little change for negative charging.

Figs.5.11 to 5.12 show dark decay rate and voltage contrast plotted against deposition rate for positive and negative charging respectively. It is seen that dark decay rate did not increase much with deposition rate for positive charging but for negative charging it decreased monotonically with deposition rate. While voltage contrast in Fig.5.12 clearly decreased with deposition rate for positive charging, it did not show much change for negative charging.

5.5 EFFECT OF CHLORINE DOPING

In order to determine the effect of chlorine in the selenium on xerographic properties, six samples were prepared with different levels of chlorine. This was done by mixing pellets of undoped selenium with selenium pellets doped with either 60 ppm or 120 ppm of chlorine by weight and placing them in a tantalum boat for evaporation. Details of the samples are given in Table 5.4. Because the concentrations in the pellets of 60 and 120 ppm were only nominal, all the chlorine concentrations given in column 2 should be regarded as approximate and relative. It should also be noted that, because of the use of a tantalum evaporation boat without temperature monitoring, the deposition rates (column 6) were higher for these samples than for the rates used for the previous samples in this chapter.

Figs.5.13 and 5.14 show the variation of acceptance voltage and residual voltage with chlorine content for positive and negative charging respectively. It is clear that both V_R and V_A decreased markedly with increase of chlorine content in selenium for both charging polarities.

Figs.5.15 and 5.16 show plots of dark decay rate and voltage contrast against chlorine concentration for positive and negative charging respectively. It is seen that the dark decay rate increased rapidly as the chlorine concentration was increased from 1 to 15 ppm for both polarities. With further increase of chlo-

rine in the selenium, it decreased for positive charging but for negative charging it remained at about the same value. The voltage contrast showed an initial decrease with chlorine content from 1 to 15 ppm, with relatively little variation with increased chlorine concentration beyond this to 90 ppm for both polarities.

5.6 VARIATION OF DARK VOLTAGE SLOPE WITH TIME

In chapter 2, it was shown that when the charge decay is controlled by progressive ionization of centres in the selenium, rather than injection of carriers from the base, a plot of dV/dt versus time t on double logarithmic scales is helpful in interpreting the decay process. Accordingly, such plots are shown in Figs.5.17 to 5.20 respectively for the effects of variations of selenium film thickness, selenium deposition temperature, selenium deposition rate and chlorine doping.

Fig.5.17 shows a plot of dV/dt versus t for six samples with different selenium thicknesses. Although no abrupt slope change was found, the plots do show a tendency towards the two-slope behavior. It is seen that the initial slopes of dV/dt, up to about 30 to 40 seconds, are less than those for the larger times from about 80 to 120 seconds. For the sample with a selenium thickness of 68 micrometers (open triangles in Fig.5.17), the initial slope corresponds to a dependence approximately of $t^{-0.6}$ and the later slope to $t^{-1.5}$. In Fig.5.18 for the samples prepared at different substrate temperatures, the curves for the 40

and 50 °C temperatures show the largest slope changes; these slopes correspond to dependencies of approximately $t^{-0.4}$ initially and t^{-1} finally. The curves for samples prepared at different selenium deposition rates in Fig.5.19 show less variation of slope. For the samples prepared at the rates of 1.4 and 3.3 micrometers per minute, the slopes correspond approximately to the dependencies $t^{-0.6}$ initially and t^{-1} finally.

Fig.5.20, for the samples with different chlorine concentrations in the selenium, shows curves with more definite slope changes. The approximate time dependencies measured from the slopes before (column 3) and after (column 4) each break point are given in Table 5.5, along with the times (t_d) to each break point.

5.7 REVIEW OF MORE PROMINENT TRENDS

In the results presented above in sections 5.2 to 5.6, some of the empirical trends were more definite than others. It is helpful to re-examine these more prominent trends.

Firstly, for variation of selenium film thickness d_p , the acceptance voltage was found to increase linearly with d_p (Fig.5.1). However, residual voltage also increased with d_p and Fig.5.21 is a re-plot of V_R against d_p but on double logarithmic scales, where V_A and dark decay are also shown for comparison. While clear linearity for V_R is not apparent in this plot, a

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straight line has been drawn through the points, corresponding to a dependence of the form, $V_R = K_1 d_p^{1.7}$, where K_1 is a constant. This dependence is not too different from the relation $V_R = q N_0 d_p^2 / 2\epsilon_0 \epsilon_r$, obtained from double integration of Poisson's equation across the selenium thickness, assuming a uniform concentration N_0 of negatively charged traps. If, however, a straight line of slope 2 is drawn through the points, a trap concentration of $N_0 \approx 10^{13}$ cm⁻³ is obtained. The fact that V_A increased as dark decay decreased with increase of selenium film thickness suggests that these two quantities are related. Accordingly from these results, V_A is plotted against dark decay rate R (%) in Fig.5.22. The straight line drawn through the points corresponds approximately to the empirical relation $V_A = -K_2R$ + K_3 , where K_2 and K_3 are constants.

The residual voltage decreased with selenium deposition temperature and Fig.5.23 shows a plot of V_R against the deposition temperature T_d (in degrees Kelvin) on semilogarithmic scales, where V_A is also plotted for comparison. It is appare t from the linearity on this plot that V_R is approximately proportional to e^{-K_4T} , where K_4 is a constant.

With increase of chlorine in the selenium, both the residual and the acceptance voltages were found to decrease. Fig.5.24 shows a semilogarithmic plot of V_R and V_A against chlorine content in the selenium for both charging polarities. The V_R variation on this plot is linear (except for the value at 1 ppm Cl), corresponding to a dependence of V_R proportional to e^{-K_5C} , where C is the chlorine concentration in ppm and K_5 is another constant. The V_A dependence, while marked, is only approximately exponential.

The observed decrease of dark decay rate with increasing chlorine content beyond 15 ppm (Fig.5.15) for positive charging is apparently in contradiction to the results of Abkowitz and Maitra^[6], who reported that dV/dt increased with Cl content in the selenium. In fact, there is no contradiction, since the present results were obtained with a constant corotron charging voltage from the high voltage power supply, whereas Abkowitz and Maitra arranged to have a constant acceptance voltage. Experiments in our laboratory (not shown) have indicated that, when a constant V_A is employed, the dark decay rate increases with chlorine content, as was found by Abkowitz and Maitra^[6].

The existence of break points in the double logarithmic plot of dV/dt versus t (Fig.5.20), suggests that in the chlorine-doped samples, the dark decay is controlled predominantly by the charge depletion model, involving the progressive ionization of centres in the selenium. If this is the case, according to Abkowitz and Maitra^[6], the time to the break point, t_d , should be proportional to the voltage V_d at the break point, which, with no loss of surface charge, should be half the initial value V_A . For the chlorine doped samples, the V_d/V_A ratios were 0.8 (1 ppm), 0.3 (15 ppm), 0.6 (30 ppm), 0.5 (60 ppm), 0.7 (90 ppm) and 0.5 (120 ppm), which deviate in some cases from the theoretical 0.5 value. Fig.5.25 is a double logarithmic plot of t_d against V_A and $2V_d$, where it is clear that t_d increased only weakly with acceptance voltage and was certainly not proportional to V_A . Fig.5.26 is a plot of t_d versus chlorine concentration, indicating that the
presence of chlorine apparently speeds up the depletion process.

According to the charge depletion model (chapter 2), the sum of the two indices of the dependencies of dV/dt on time t before and after the break point should be -2. Accordingly, in Table 5.5, column 5 gives the sum of these indices from the experimental results. While the values are not -2, the average value is about -1.8.

5.8 **DISCUSSION**

The decrease of dark decay rate with increase of acceptance voltage as the selenium film thickness is changed (Fig.5.22) is not difficult to understand. The acceptance voltage is the voltage at which the charging and discharging rates are equal initially. Thus, if the charging rate is constant, because of the constant corotron voltage, the initial voltage will be lower if the discharge rate is higher. The relation between V_A and dV/dt, however, may be more complex when changes to the selenium are made via substrate temperature or chlorine content variation. The linear increase of V_A with thickness (Fig.5.1) reflects the fact that the initial electric field in the selenium must be constant. Thus, as the thickness of the selenium is increased, the voltage drop across it is increased proportionately.

The increase of residual voltage with selenium film thickness is nearly quadratic (Fig.5.21) and this is consistent with a uniform distribution of negatively charged traps, estimated to have a concentration of the order of 10^{13} cm⁻³ in the undoped

selenium.

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As explained in section 5.7, the dark decay rate actually would have been increased with chlorine content if the same acceptance voltage had been maintained. The observed decrease of V_A with chlorine (Fig.5.13) is thus due to this increase of decay rate. It is presumed that the higher decay rate results from a lowering of the electrical resistivity of the selenium with increased chlorine content. The fact that the residual voltage also decreased with chlorine content (Fig.5.13) suggests that the chlorine causes the concentration of trapping centres to decrease. This might happen, for instance, if the chlorine atoms attached themselves to the Se chain ends, which, if left as dangling bonds could act as trapping centres.

The decrease of residual voltage with increase of selenium substrate temperature (Figs.5.5 and 5.23) suggests that the higher temperature causes a decrease in the concentration of trapping centres. This may be the result of a lengthening of the chains of Se atoms with a corresponding decrease in the number of dangling bonds. The observed minimum of decay rate with increase of deposition temperature (Fig.5.7) is not easily explained. However, it is of interest to note that V_A had a maximum at the same temperature as the decay rate minimum.

With increase of selenium deposition rate, the observed trends were not very definite. However, the possible slight increase in residual voltage (Fig.5.9) may indicate that a faster deposition rate generates a higher concentration of trapping centres.

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Sample	Se film	Weight of Se	Subs.	Source	Dep.	Dep.
	thickness	pellets charged	temp.	temp.	time	rate
No.	(µm)	(gram)	(°C)	(°C)	(min)	(µm∕min)
Z051	10	1	50	260	12	0.83
Z050	18	2	50	260	20	0.90
Z052	42	4	50	260	35	1.20
Z053	50	6	50	260	40	1.25
Z054	68	8	50	260	55	1.24
Z055	80	10	50	260	60	1.33

Samples with different Se film thicknesses

Note: Aluminum substrates were oxidized by air-heating at 400°C⁻ for 2 hours.

Table 5.2

Samples prepared with different substrate temperatures

Sample No.	Subs. temp. (°C)	Se film thickness (µm)	Source temp. (°C)	Dep. time (min)	Dep. rate (µm/min)
2056	30	55	260	40	1.37
2057	40	55	260	45	1.22
2053	50	50	260	40	1.25
2058	60	45	260	50	0.90
2059	70	45	260	50	0.90

Note: Aluminum substrates were oxidized by air-heating at 400°C for 2 hours.

Table 5.3 Samples prepared with different selenium deposition rates

Sample No.	Se dep. rate (µm/min)	Subs. temp. (°C)	Source temp. (°C)	Se film thickness (µm)	Dep. time (min)
Z048	0.56	50	240	45	80
Z047	0.67	50	250	50	75
Z044	1.0	50	260	45	45
Z045	1.28	50	270	45	35
Z046	1.40	50	280	42	30
Z049	3.20	50	300	48	15

Note: Aluminum substrates were oxidized by air-heating at 400°C for 2 hours.

Table 5.4 Samples prepared with different dopant concentrations of chlorine

Sample No.	Chlorine content (ppm)	Se film thickness (µm)	Subs. temp. (°C)	Dep. time (min)	Dep. rate (µm/min)
Z001	1	50	50	10	5.0
Z007	15	50	50	15	3.3
Z006	30	50	50	15	3.3
Z002	60	50	50	13	3.8
Z005	90	50	50	16	3.1
Z004	120	50	50	10	5.0

- Note: 1) Aluminum substrates were oxidized by air-heating at 400°C for 2 hours.
 - 2) Boat used in this experiment was made from tantalum sheet. Source temperature was not measured.
 - 3) The chlorine concentrations given in column 2 are nominal values for the source material.

Table 5.5

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Variation of slope and t_d for log(dV/dt) versus log(t) plots of samples prepared with different chlorine concentrations in the selenium

	Chlorine content (ppm)	Slop			
Sample No.		Initial	Final	Sum of initial and final t exponents	slope change (sec)
Z001 Z007 Z006 Z002 Z005 Z004	1 15 30 60 90 120	t-0.7 t-1.1 t-0.7 t-0.6 t-0.26 t-0.2	$t^{-1.1}$ $t^{-2.0}$ $t^{-1.3}$ $t^{-1.2}$ $t^{-1.2}$ $t^{-0.6}$	-1.8 -3.1 -2.0 -1.8 -1.46 -0.8	110 85 90 80 65 60







Fig. 5.2 Acceptance and residual voltage plotted against selenium thickness for selenium plates deposited at a substrate temperature of 50°C and charged negatively

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plates deposited at a substrate temperature

of 50°C and charged positively





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against substrate deposition temperature for selenium films of thickness 50 um for negative charging



Fig. 5.7 Plot of dark decay rate and voltage contrast against substrate deposition temperature for selenium films of thickness 50 um for positive charging



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Fig. 5.9 Acceptance and residual voltage plotted against selenium deposition rate for positive charging. The selenium substrate temperature and thickness were 50°C and 50 µm respectively



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Negative Charging

Se Deposition Rate (,um/min)

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0

3

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Fig. 5. 12 Dark decay rate and voltage contrast plotted against selenium deposition rate for negative charging. The selenium substrate temperature and thickness were 50°C and 50 um respectively



Fig.5.13 Acceptance and residual voltage plotted against chlorine concentration in Se for positive charging. The selenium substrate temperature and thickness were 50°C and 50µm respectively. Fig.5.14 Acceptance and residual voltage plotted against chlorine concentration in Se for negative charging. The selenium substrate temperature and thickness were 50°C and 50µm respectively.

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Fig.5.15 Dark decay rate and voltage contrast plotted against chlorine concentration in Se for positive charging. The selenium substrate temperature and thickness were 50°C and 50µm respectively.



Fig.5.16 Dark decay rate and voltage contrast plotted against chlorine concentration in Se for negative charging. The selenium substrate temperature and thickness were 50°C and 50µm respectively.

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Fig.5.17 Log-log plot of dV/dt versus time t for samples with different Se film thicknesses for positive charging.

Fig.5.18 Log-log plot of dV/dt versus time t for samples prepared with different substrate temperatures for positive charging.

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Fig.5.19 Log-log plot of dV/dt versus time t for samples prepared with different selenium deposition rates for positive charging.

Fig.5.20 Log-log plot of dV/dt versus time t for samples prepared with different dopant concentrations of chlorine for positive charging.



Fig.5.21 Replot of acceptance and residual voltage (V_A and V_R) versus selenium film thickness on log-log scales (left side). Dark decay rate versus selenium film thickness replotted on linear-log scales (right side) for comparison.



Fig.5.22 Acceptance voltage (data from Fig.5.1) replotted against dark decay rate (data from Fig.5.3) for selenium films deposited at a substrate temperature of 50°C and charged positively.



Fig.5.23 Replot of residual and acceptance voltage against selenium deposition temperature (in degrees Kelvin) on semilogarithmic scales for selenium films of thickness 50 µm with positive charging.



Fig.5.24 Replot of residual and acceptance volttage against chlorine content in selenium on semilogarithmic scales with both positive and negative charging. The selenium substrate temperature and thickness were 50°C and 50µm respectively.



Fig.5.25 Dependence of the depletion time t_d on the acceptance voltage V_A and twice the depletion voltage $2V_{td}$ for samples prepared with different dopant concentrations of chlorine with positive charging.





Chlorine Content (ppm)

Fig.5.26 Depletion time t_d plotted against chlorine content in the selenium for positive charging. The selenium substrate temperature and thickness were 50°C and 50µm respectively.

CHAPTER 6 EFFECT OF OXIDE INTERMEDIATE FILM

6.1 INTRODUCTION

In the xerographic process it is necessary that the surface charge on the selenium should not leak away too rapidly before illumination. It was found by the early developers of the xerographic process that the presence of a thin film aluminum oxide between the selenium film and the aluminum base was helpful in reducing the dark discharge rate. This oxide can be created in many different ways as described in chapter 3. In the present chapter the results of the different methods are evaluated in terms of the xerographic parameters described in chapter 4. One of the methods, d.c. glow discharge appears to be a standard procedure in the photoreceptor industry. This method is compared principally with oxidation by d.c. reactive sputtering and with thermal oxidation in this chapter.

6.2 RESULTS OF REACTIVE SPUTTERING

The d.c. reactive process to create the aluminum oxide film was described in chapter 3. This process has the advantages of convenient control, the use of high purity aluminum only in the target and the ability to obtain much greater thicknesses than other methods. Details of the fabrication of the samples prepared by d.c. reactive sputtering are given in Table 6.1, where it is seen that the sputtering times employed ranged from 3 to 360 minutes. For the same sputtering time, two samples each were prepared; one consisted of the oxidized aluminum film with the supplemental 50 micrometer selenium layer deposited on it at a substrate temperature of 50°C on which the xerographic measurements were made; the other sample consisted of the oxide on the aluminum alone plus the small Wood's metal areas for capacitance and resistance measurements.

(a) Measurements on Samples with Selenium Layer

The results of measurements made on samples consisting of an oxidized aluminum plate coated with selenium are now given.

(i) Variation with oxide thickness

Figs.6.1 to 6.8 show the variation with oxide thickness of acceptance voltage V_A , residual voltage V_R , dark decay rate and voltage contrast, as defined in section 4.2(e). Figs.6.1 and

Fig.6.2 show generally that V_A decreased with oxide thickness with little difference between the positive and negative charging of the selenium film. However, the residual voltage V_R (Figs.6.3 and 6.4) was much greater for negative charging. Furthermore, V_R did not vary much with oxide thickness for positive charging but generally showed a strong decrease with negative charging. The dark decay rate (Figs.6.5 and 6.6) was lower for negative charging than positive charging, but for both polarities, a clear trend with oxide thickness was not apparent. The voltage contrast in Fig.6.7 for positive charging was larger than that for negative charging (Fig.6.8), at least with thicknesses up to about 1000Å.

(ii) Variation with oxygen content

Figs.6.1 to 6.8 also show the results for three gas environments during the sputtering. It is noted that the $5\$0_2+95\Ar composition for positive charging gave generally the lowest values of V_A and voltage contrast and the highest dark decay rate. However, it also gave low values of residual voltage, particularly for negative charging. For the samples prepared in air and in $50\$0_2+50\Ar , the values of V_A , V_R , dark decay rate and voltage contrast were somewhat similar.

(iii) Variation of dark voltage slope with time

Figs.6.9 to 6.11 show plots of dV/dt versus time t on double logarithmic scales for the three gas compositions $5\%0_2$, $50\%0_2$ and air . Here V is the voltage on the selenium film measured during the dark decay.

It is seen that, while the magnitude of dV/dt decreases with time, the initial slope of dV/dt, up to about 50 seconds, is generally less than that for larger times. In some cases the variation appears to consist of two straight lines meeting at an inflection point. This is exemplified, for example, in Fig.6.11 by the sample fabricated with a 30-minute sputtered oxide film in air. Up to about 70 seconds, dV/dt was approximately proportional to $t^{-0.3}$ and for t greater than 70 seconds, it was proportional approximately to $t^{-1.5}$. However, for the most part, the variations in Fig.6.11 do not exactly follow this pattern. One would expect from the theory that the samples with the lowest initial decay rates would also show the two-slope behavior but, in fact, this behavior is more apparent in the samples with higher dV/dt values, where carrier injection from the base would be expected to be dominant. Thus, the mechanism of decay by recombination centres in lower decay-rate samples has not been confirmed.

(b) Measurements on Oxide Film Samples

The results of measurements of incremental parallel capacitance and resistance with variation of frequency between 100Hz and 1MHz are shown in Figs. 6.12 to 6.14 on double logarithmic scales.

(i) <u>Capacitance</u>

Little variation of capacitance with frequency is noted, so that values of this quantity can be used to determine the oxide

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thicknesses. Accordingly, Fig.6.15 shows a plot of oxide thicknesses, determined from capacitance, plotted against sputtering time. It is noted that the oxide growth rate decreases with sputtering time.

(ii) Resistance

Figs. 6.12 to 6.14 show that the resistance decreases with frequency. This can be quantitatively explained if the equivalent circuit of the oxide can be considered to consist of a capacitor-resistor parallel combination in series with another resistor of lower value. In this case, the lower frequency resistance values could arise from leakage current through the oxide film. In general, it is noted that the resistance values increase with sputtering time, especially at low frequency. At 100Hz the resistance values, for a sputtering time of 30 minutes or more, lie between 10^7 and 10^8 ohm, which are more than two orders of magnitude higher than the resistances found for the oxides formed by thermal oxidation and glow discharge.

6.3 RESULTS OF THERMAL OXIDATION

Direct oxidation by heating the aluminum substrate in oxygen or air was also used to form the interfacial barrier of aluminum oxide between the aluminum base and the selenium layer. This procedure has the advantage of being a simple process which is controlled mainly by the substrate temperature. Although thermal-

ly produced oxide films are thinner (ranging from 50 to 210 Å in this study) than can be produced by d.c. reactive sputtering, they are sufficiently thick for the blocking action required between the selenium film and the aluminum substrate. Three variations of thermal oxidation were used in the present study, namely air heating, vacuum heating and heating in oxygen after degassing under vacuum pumping. These method variations are described in sections 3.3 and 3.6. Table 6.2 summarizes the thermal oxidation processes used. As in section 6.2, two sets of samples were prepared for each oxidation run, one with the selenium layer for xerographic measurements and the other without the selenium for thickness determination by capacitance measurements.

(a) Measurements on Samples with Selenium Layer

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Figs.6.16 to 6.23 show the results of xerographic measurements on plates thermally oxidized and then coated with a layer of selenium.

(i) Variation with oxidation treatment and oxide thickness

From Figs. 6.16 and 6.17, a clear trend of acceptance voltage V_A with increase of oxide thickness is not apparent. However, for positive charging the air-heated samples gave the highest V_A values and the vacuum-heated ones the lowest values. By contrast, for residual voltages (Figs. 6.18 and 6.19), the vacuumheated samples gave the lowest values for either positive or negative charging. For both polarities, V_R decreased with oxide thickness for the air-heated samples. The dark decay rates (Figs. 6.20 and 6.21) were much lower for the air-heated and degassed-

heated samples than the vacuum-heated samples for positive charging. For negative charging, the dark decay rates were low with about the same values for all three oxidation processes. The voltage contrast values (Figs. 6.22 and 6.23) for the air-heated and vacuum-heated samples increased with oxide thickness and were higher than for the degassed-heated samples for positive charging.

It is clear from these measurements that the air-heated samples gave the best overall xerographic performance, considering their high voltage contrast values and acceptance voltages and their low dark decay rates. However, they did not show the lowest residual voltages but this quantity did decrease to a lower value with increased thickness up to 210 Å. The other feature, which comes from the measurements, is that the degassed-heated samples did not show an improvement over the samples heated in air, without the prior degassing treatment. While the vacuum-heated samples showed low residual voltages, they also showed lower dark decay rates but only for negative charging.

(ii) Variation of dark voltage slope with time

Figs.6.24, 6.25 and 6.26 show plots of dV/dt versus time t on double logarithmic scales. In general, dV/dt decreased with time t at roughly a constant rate up to 60 to 100 seconds and then it decreased more rapidly. The characteristic of having a break point was generally more evident in samples with larger dV/dt values. For instance, the sample where the oxide was prepared by air heating at 200°C (solid circles in Fig.6.24), the

initial slope of dV/dt was approximately proportional to $t^{-0.5}$ but after the break point at 100 seconds, it varied approximately as t^{-2} . This type of dependence, however was less in evidence in other samples.

(b) Measurements on Oxide Film Samples

Measurements of capacitance and resistance were made on samples consisting of aluminum plates thermally oxidized with small evaporated areas of Wood's metal.

(i) Capacitance

Plots of parallel capacitance and resistance against frequency are shown in Figs.6.27, 6.28 and 6.29. These measurements were more difficult to carry out than those on the thicker films prepared by reactive sputtering, particularly at low frequency. It is noted that while the capacitance for the air-heated samples was independent of frequency, the values for the degassed-heated and vacuum-heated samples decreased with frequency, particularly above 10 to 100 kHz. Never-the-less, the low frequency capacitance values were used to calculate the oxide thicknesses. Fig.6.30 shows a plot of oxide thickness plotted against oxidation time for the degassed-heated samples, where it is noted that the thickness tends to saturate beyond a heating time of about 200 minutes at a thickness of about 180 Å. Fig.6.31 shows a plot of oxide thickness against oxidation temperature for airheated and vacuum-heated samples. There is again a tendency for the thickness to saturate but in this case it is beyond a temperature of 500°C at thickness values above 200 Å. These plots

suggest that thermal oxidation is only suitable for making oxide films up to thicknesses of 200-300 Å.

(ii) Resistance

Figs.6.27 to 6.29 show that plots of resistance against frequency exhibit similar trends to those samples prepared by d.c. reactive sputtering but with a plateau at low frequencies. The values of resistance at this frequency, however, are seen to be about 2 to 3 orders of magnitude smaller. This may arise from the much thinner oxide films produced by thermal oxidation compared with reactive sputtering.

6.4 RESULTS OF OXIDATION BY D.C. GLOW DISCHARGE WITH SAMPLE A'T CATHODE AND A.C. GLOW DISCHARGE

Apart from oxidation by d.c. reactive sputtering (section 6.2), other glow discharge processes were also investigated. Two of these were: oxidation in an a.c. (60 Hz) glow discharge and oxidation with the aluminum plate located at the cathode (i.e. at the "target" position) during a d.c. glow discharge. Details of these oxidation procedures are given in section 3.6 of chapter 3. As with the previous methods described in this chapter, two samples were prepared in each experimental run, one with a selenium layer for xerographic measurements and the other without the selenium for capacitance measurements.

(a) Measurements on Samples with Selenium Layer

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The results of measurements on samples oxidized in an a.c. glow discharge and in a d.c. glow discharge with the plate at the cathode are now described.

(i) Variation with oxidation treatment and oxide thickness

Fig.6.32 shows that the acceptance voltage for the a.c. glow discharge samples increased with increasing oxide thickness for positive charging and, at a thickness of 150 Å, was greater than the values for negative charging (Fig.6.33). For the cathodic discharge samples, acceptance voltages were lower for both polarities. While the residual voltages (Figs.6.34 and 6.35) were not significantly different between the two glow discharge methods for positive charging, they were much larger for the a.c. discharge samples for negative charging and increase? /ith oxide thickness. The dark decay rates for negative charging (Fig.6.37) were lower than those for positive charging (Fig.6.36) and showed little variation with oxide thickness. The voltage contrast values (Figs.6.38 and 6.39) increased with increase of oxide thickness for positive charging for the a.c. discharge samples but showed the opposite trend for negative charging. From Figs.6.32 to 6.39, it is noted that the range of oxidation thicknesses obtained with the cathodic discharge method was rather small and hence no clear trend of its xerographic characteristics with thickness can be discerned.

(ii) Variation of dark voltage slope with time

Figs.6.40 and 6.41 give the results of dark voltage slope dV/dt plotted against decay time t on double logarithmic scales. For the a.c. discharge samples (Fig.6.40), there was no pronounced slope change of dV/dt with time but for the cathodic discharge samples, a two-slope behavior is more apparent, with a break-point generally near 100 seconds. In the case of the cathodic discharge sample oxidized for 30 minutes (solid circles in Fig.6.41), the initial slope of dV/dt corresponded approximately to a $t^{-0.5}$ dependence, with a dependence after the break-point of approximately $t^{-1.7}$.

(b) Measurements on Oxide Film Samples

Fig.6.42 and Fig.6.43 show plots of parallel capacitance and resistance versus frequency on double logarithmic scales. It is noted that the resistance values for the a.c. glow discharge samples (Fig.6.42) at low frequency are larger than those obtained on samples prepared by thermal oxidation (Figs.6.27 to 6.29) for the same oxide thickness range. The resistance values are, in fact, comparable to those obtained with d.c. reactive sputtering (Figs.6.12 to 6.14), where the oxide was an order of magnitude thicker. The capacitance values, which varied little with frequency, were used to calculate oxide thicknesses. For the cathodic discharge samples, the resistance values were some four orders of magnitude smaller, with a plateau at low frequency. The capacitance for the a.c. discharge samples did not vary with frequency but the results for the cathodic discharge samples

showed a fall-off at higner frequency. It may also be noted that, while the resistance for both methods increased with glow discharge time, the capacitance of the cathodic discharge samples showed little variation with discharge time.

6.5 RESULTS OF GLOW DISCHARGE

A method often used in industry to form the oxide films is a d.c. glow discharge technique, where the aluminum base is located at the anode, similar to that used in the d.c. reactive sputtering method described earlier in section 6.2. However, the glow discharge voltage in this method is smaller and the cathode-toanode distance is larger. Accordingly, some preliminary samples were made to test this method.

(a) Formation of Oxide Films

In this process, the same arrangements were used as in the reactive sputtering method but with an anode-to-cathode separation twice as large and an applied voltage half as much. To test whether reactive sputtering was suppressed, an experiment was carried out whereby the sample at the anode consisted of a glass microscope slide coated over half of its area with an evaporated aluminum film. After a discharge of 40 hours, a thin transparent aluminum film was evaporated over the two parts of the slide. Oxide was found to be formed on the aluminum film with a thick-ness large enough to see interference colors — possibly 2000 Å.

However, on the part of the glass not previously coated with the metal, no interference was seen, indicating no oxide. Thus no discernible sputtering of the aluminum took place from the target (cathode) on to the substrate at the anode.

(b) Xerographic Measurements

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Six oxide-coated aluminum plates were made by this method and coated with the usual layer of about 50 micrometers of selenium. No attempt was made in these preliminary experiments to vary the oxide thickness or to measure its value by capacitance. All six samples were found to give essentially the same variation of dark potential with time after positive and negative charging (not shown). However, two of the samples were etched differently prior to oxidation; one was etched with etch "a" (see section 3.2) and the other with etch "b". Two other samples were prepared, neither of which was oxidized before selenium deposition but one was etched with etch "a" and the other with etch "b". Fig.6.44 shows the variations of potential with time after positive charging for these four samples. It is noted that for the unoxidized sample etched with etch "b", the acceptance voltage was lower and the dark decay rate larger than the unoxidized sample etched with etch "a". However, it is also seen that for the two oxidized samples, the dark decay rate and acceptance voltage were about same, despite the different etchants used. Thus, the oxidation by the d.c. glow discharge action has the beneficial effect of correcting any deleterious effects of the etching of the aluminum.

(c) Variation of Dark Voltage Slope with Time

The variation of dV/dt with time t for the four d.c. glow discharge samples of Fig.6.44 is shown in Fig.6.45 on double logarithmic scales. It is noted that for the two samples without an oxide film the experimental points do not show a two-slope dependence. However, for the samples with an oxide film, there is a tendency towards a two-slope behavior with a breakpoint near 50 seconds. For the results with the solid triangular points in Fig.6.45, the dependence up to 50 seconds was approximately $t^{-0.4}$ and that beyond 50 seconds approximately $t^{-0.7}$.

(d) Measurements On Oxide Film Sample

Fig.6.46 shows incremental parallel capacitance and resistance plotted against frequency on double logarithmic scales. The capacitance decreased only slightly with frequency and yielded an oxide thickness of 280 Å. The resistance also showed little variation up to 100 kilohertz, with a decrease above this frequency. It may be noted that the magnitude of the resistance was much lower than that observed for reactive sputtering and thermal oxidation.

6.6 DISCUSSION OF RESULTS

In order to compare the results of the different oxidation methods, some important experimental values are compared in Table 6.3. From this table, it is clear that the d.c. glow discharge

and the thermal air oxidation methods give the best xerographic results, with the former being slightly better. Oxidation by d.c. reactive sputtering is satisfactory but not as good as the two just mentioned. This method can produce much thicker oxide layers, of the order of a few thousand angstroms than the other methods, which yielded layers of only a few hundred angstroms. Never-the-less, the results show no benefit xerographically in having thicker layers, although this has been helpful for checking that the capacitance measurements give reliable thickness values. It may well be that the effectiveness of films by d.c. reactive sputtering should be re-examined specifically for thicknesses in the range 0 to 200 Å. In the thermal oxidation process, prior degassing of the aluminum did not seem to be helpful, even though originally such a treatment seemed to offer the apparent advantage of eliminating any oxide formed from residual oxygen within the plate. Thermal oxidation under reduced pressure also did not yield good results. Nor did oxidation by d.c. glow discharge with the sample located at the cathode, which was accompanied by etching through ionic bombardment. While the xerographic behavior for oxides prepared by a.c. glow discharge was also poor, it should be borne in mind that these were the earliest experiments, where an un-optimized glow discharge arrangement was employed. It would seem that, since d.c. glow discharge oxidation yielded good results, a.c. glow discharge should do the same.

For all the oxidation methods, it was found that the acceptance voltage was higher for positive charging than negative charging. This polarity dependence indicates nonsymmetric block-

ing action for the intermediate oxide layer, which could arise from a Schottky barrier between the aluminum oxide and the aluminum or a heterojunction between the oxide and the selenium.

Apart from the above considerations, the results of this chapter clearly show the benefit of the interfacial oxide film. Without it, xerographic performance is poor, with low acceptance voltage and large dark decay. The present results also show that the type of prior etching of the aluminum may not be important, since the results with two different types of etching without the oxide were very different but after oxidation the structures yielded the same improved xerographic behavior.

	sputter.	2				
Sam- ple No.	gas composition	sputt. press. (mT)	sputt. volt. (V)	sputt. time (min)	separ ¹ dist. (cm)	thick- ness (Å)
Z092 Z068 Z067 Z066 Z069 Z070	5%0 ₂ +95%Ar 5%0 ₂ +95%Ar 5%0 ₂ +95%Ar 5%0 ₂ +95%Ar 5%0 ₂ +95%Ar 5%0 ₂ +95%Ar	40 40 40 40 40 40	2000 2000 2000 2000 2000 2000	3 15 30 60 180 360	5 5 5 5 5 5 5	280 610 860 1290 2350 3130
2091 2078 2079 2081 2080 2082	air air air air air air	80 80 80 80 80 80 80	1200 1200 1200 1200 1200 1200	3 15 30 60 180 360	4 4 4 4 4	240 640 880 1290 2180 3000
Z085 Z086 Z087 Z088 Z089 Z090	$50\%0_{2}+50\%Ar$ $50\%0_{2}+50\%Ar$ $50\%0_{2}+50\%Ar$ $50\%0_{2}+50\%Ar$ $50\%0_{2}+50\%Ar$ $50\%0_{2}$ +50%Ar	50 50 50 50 50 50	1000 1000 1000 1000 1000 1000	3 15 30 60 180 360	4 4 4 4 4	320 500 880 1400 2310 3180

Table 6.1 Samples prepared by reactive sputtering

- 1/ Distance from aluminum target (cathode) to sample
 (anode).
- 2/ Thickness determined by capacitance.

Com			Oxidat	Ovido		
ple Nc.	Methods	Oxidation process	Equipment used	Heating temp. (°C)	Heating time (hour)	thick- ness (Å)
Z031 Z032 Z033 Z034 Z036	Air heated	Heated in tube furnace in air at normal pressure for the temperature indicated.	Tube furnace	100 200 300 400 500	2 2 2 2 2 2	90 130 160 180 210
Z039 Z035 Z037 Z038	Vacuum heated	Heated at about 5 millitorr pressure in flowing oxygen at the temperature indicated.	Vacuum system	50 100 200 300	2 2 2 2	50 90 120 180
Z093 Z097 Z096 Z095 Z094	Vacuum degassed & heated	Heated at 200°C in flowing oxygen at atmospheric pressure after degassing by heating up to 200°C under vacuum for the time indicated.	Vacuum system	200 200 200 200 200	0.5 1 2 3 4	90 130 160 180 190

Table 6.2 Samples prepared by thermal oxidation

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Optimum and Average Values of Xerographic Characteristics for Different Oxidation Treatments

		Optimum Values							Average Values						
		Oxide Depos.			Characteristics				Oxide Depo	Characteristics				Overall	
Oxidation Methods	Conditions	Time or Temp.	Oxic Thic ness	le ck-	v _A ¹ (V)	v _R ² (V)	3 (%)	4 <u>V</u> 2 V _R	Time or Temp	Oxide Thickness (Å)	V _A ¹ (∨)	v _R ² (∨)	3 (%)	4 <u>V</u> 2 V _R	performance
D.C. Reactive Sputtering	5%0 ₂ +95%Ar	3mın	275	Å	740	16	7.6	43	3min-3hr	250-2300	450	25	25	22	Satisfactory
	50%0 ₂ +50%Ar	15min	500	Å	780	17	4.4	45	3mın-3hr	250-2300	720	17	12	22	
	Air	30min	880	Å	730	14	7	49	3mın-3hr	250-2300	650	10	12	52	
Thermal Oxidation	Air heating	400°C	180	Å	830	22	5	35	200-500°C	150-250	800	20	15	35	Very good
	Degas-heating	3hr	175	Å	520	16	13	28	30min-4hr	90-180	600	20	20	23	Satisfactory
	Vac. Heating	100°C	90	Å	650	7	45	51	100-300°C	80-18u	450	7	65	40	Poor
D.C. Glow Discharge	Air	15min	240	Å	800	10	4	70	15min	120-240	790	15	5	50	Very good
Other Glow Discharge Methods	A.C.	3hr	150	Å	680	9	14	65	30min-3hr	50-150	400	7	40	30	Poor
	D.C.Cathodic ⁵	30min	140	Å	450	9	19	38	30min-2hr	140-170	300	5	30	35	Poor
Anodizing ⁶	Not know	vn 2.2µm		535	52	38	6.4	-	-	-	-	-	-	-	
No Oxidation (Fresh Al Surface)	Etching a ⁷	-	-	- (9	31	48	-	-	600	10	30	35	Poor
	Etching b ⁷	_	-		270	6	78	10	-	-	290	6	80	10	

1480 C

- 1/ V_A : acceptance potential, as defined in chapter 4;
- 2/ V_R : residual potential, as defined in chapter 4;
- 3/ % : dark decay rate, as defined in chapter 4;
- 4/ Voltage contrast, as defined in chapter 4;
- 5/ D.C. glow discharge with pure aluminum anode and sample mounted at cathode.
- 6/ Aluminum plate oxidized by anodizing, as supplied by external laboratory.
- 7/ Aluminum substrates were cleaned ultrasoniclly by immersion for 10 minutes each in ethvl alcohol and acetone. They were then treated by one of the following: a : etching in chromic/phosphoric acid at 90°C for 10 minutes;
 - b : etching in sodium carbonate/sodium orthophosphate at 65°C for 1.5 minutes, then etching in HNO₃ for 1 minute.



Fig.6.1 Acceptance voltage plotted against oxide thickness for samples oxidized by reactive sputtering and charged positively. The selenium substrate temperature and thickness were 50°C and 50µm respectively.

NEGATIVE CHARGING



Fig.6.2 Acceptance voltage plotted against oxide thickness for samples oxidized by reactive sputtering and charged negatively. The selenium substrate temperature and thickness were 50°C and 50µm respectively.



Fig.6.3 Residual voltage plotted against oxide thickness for samples oxidized by reactive sputtering and charged positively. The selenium substrate temperature and thickness were 50°C and 50µm respectively.

NEGATIVE CHARGING



Fig.6.4 Residual voltage plotted against oxide thickness for samples oxidized by reactive sputtering and charged negatively. The selenium substrate temperature and thickness were 50°C and 50µm respectively.



Fig.6.5 Dark decay rate plotted against oxide thickness for samples oxidized by reactive sputtering and charged positively. The selenium substrate temperature and thickness were 50°C and 50µm respectively.

60 -0- 50% 0+50% Ar -0- Air -0- 5% 0+95% Ar 20 -0- 5% 0+95% Ar

Fig.6.6 Dark decay rate plott d against oxide thickness for samples oxidized by reactive sputtering and charged negatively. The selenium substrate temperature and thickness were 50°C and 50µm respectively.

Oxide Thickness

2000

(A)

3000

1000

0



Fig.6.7 Voltage contrast plotted against oxide thickness for samples oxidized by reactive sputtering and charged positively. The selenium substrate temperature and thickness were 50°C and 50µm respectively.



Fig.6.8 Voltage contrast plotted against oxide thickness for samples oxidized by reactive sputtering and charged negatively. The selenium substrate temperature and thickness were 50°C and 50µm respectively.



50% O₂+50% Ar

6 hr

3 hr

1 hr

1 1 1 1 1

30 min

🛦 15 mm

🕷 3mm

n ^{′օ}դ_{դյ}

200

100



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Fig 6.11 Log-log plot of dV/dt versus time t for mamples prepared with different sputter-ing times in air and charged positively.

5% O₂+95% Ar



Fig.6.12 Resistance and capacitance plotted against frequency for samples prepared with different sputtering times in 5%0₂+95%Ar on log-log scales. The area for measurement was 0.071 cm².

Fig.6.13 Resistance and capacitance plotted against frequency for samples prepared with different sputtering times in 50%0₂+50%Ar on log-log scales. The area for measurement was 0.071 cm².



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Fig.6.14 Resistance and capacitance plotted against frequency for samples prepared with different sputtering times in air on log-log scales. The area for measurement was 0.071 cm².



Fig.6.15 Oxide thickness plotted against sputtering time for samples prepared in three gas environments. Oxide thicknesses were measured by the capacitance method.



Fig.6.16 Acceptance voltage plotted against oxide thickness for samples prepared by thermal oxidation and charged positively. The selenium substrate temperature and thickness were 50°C and 50µm respectively.



Fig.6.17 Acceptance voltage plotted against oxide thickness for samples prepared by thermal oxidation and charged negatively. The selenium substrate temperature and thickness were 50°C and 50µm respectively.



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Fig.6.18 Residual voltage plotted against oxide thickness for samples prepared by thermal oxidation and charged positively. The selenium substrate temperature and thickness were 50°C and 50µm respectively.



Fig.6.19 Residual voltage plotted against oxide thickness for samples prepared by thermal oxidation and charged negatively. The selenium substrate temperature and thickness were 50°C and 50µm respectively.



Fig.6.20 Dark decay rate plotted against oxide thickness for samples prepared by thermal oxidation and charged positively. The selenium substrate temperature and thickness were 50°C and 50 µm respectively.

NEGATIVE CHARGING



Fig.6.21 Bark decay rate plotted against oxide thickness for samples prepared by thermal oxidation and charged negatively. The selenium substrate temperature and thickness were 50°C and 50 µm respectively.

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Fig.6.22 Voltage contrast plotted against oxide thickness for samples prepared by thermal oxidation and charged positively. The selenium substrate temperature and thickness were 50°C and 50 µm respectively.

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Fig.6.23 Voltage contrast plotted against oxide thickness for samples prepared by thermal oxidation and charged negatively. The selenium substrate temperature and thickness were 50°C and 50 µm respectively.



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Fig.6.27 Refistance and capacitance plotted against frequency for air-heated samples with different heating temperatures on log-log scales. The area for measurement was 0.018 cm².



Fig.6.28 Resistance and capacitance plotted against frequency for degassed-heated samples with different heating times on log-log scales. The area for measurement was 0.018 cm².

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Fig.6.29 Resistance and capacitance plotted against frequency for vacuum-heated samples with different heating temperatures on log-log scales. The area for measurement was 0.018 cm².



Fig.6.30 Oxide thickness plotted against heating time for degassed-heated samples. Oxide thicknesses were measured by the capacitance method.





Fig.6.31 Oxide thickness plotted against heating temperature for air-heated and vacuumheated samples. Oxide thicknesses were measured by the capacitance method.



Fig.6.32 Acceptance voltage plotted against oxide thickness for samples prepared by a.c. glow discharge and d.c. glow discharge with sample at cathode and charged positively. The selenium substrate temperature and thickness were 50°C and 50 µm respectively.



Fig.6.33 Acceptance voltage plotted against oxide thickness for samples prepared by a.c. glow discharge and d.c. glow discharge with sample at cathode and charged negatively. The selenium substrate temperature and thickness were 50°C and 50 µm respectively.



Fig.6.34 Residual voltage plotted against oxide thickness for samples prepared by a.c. glow discharge and d.c. glow discharge with sample at cathode and charged positively. The selenium substrate temperature and thickness were 50°C and 50 µm respectively.



Fig.6.35 Residual voltage plotted against oxide thickness for samples prepared by a.c. glow discharge and d.c. glow discharge with sample at cathode and charged negatively. The selenium substrate temperature and thickness were 50°C and 50 µm respectively.



Fig.6.36 Dark decay rate plotted against oxide thickness for samples prepared by a.c. glow discharge and d.c. glow discharge with sample at cathode and charged positively. The selenium substrate temperature and thickness were 50°C and 50 µm respectively.



Fig.6.37 Dark decay rate plotted against oxide thickness for samples prepared by a.c. glow discharge and d.c. glow discharge with sample at cathode and charged negatively. The selenium substrate temperature and thickness were 50°C and 50 µm respectively.



Fig.6.38 Voltage contrast plotted against oxide thickness for samples prepared by a.c. glow discharge and d.c. glow discharge with sample at cathode and charged positively. The selenium substrate temperature and thickness were 50°C and 50 µm respectively.



Fig.6.39 Voltage contrast plotted against oxide thickness for samples prepared by a.c. glow discharge and d.c. glow discharge with sample at cathode and charged negatively. The selenium substrate temperature and thickness were 50°C and 50 µm respectively.



Fig.6.40 Log-log plot of dV/dt versus time t for samples prepared by a.c. glow discharge with different times for positive charging. Fig.6.41 Log-log plot of dV/dt versus time t for samples prepared by d.c. glow discharge with sample at cathode with different times for positive charging.



Fig.6.42 Resistance and capacitance plotted against frequency for samples prepared by a.c. glow discharge with different times on log-log scales. The area for measurement was 0.018 cm².



Fig.6.43 Resistance and capacitance plotted against frequency for samples prepared by d.c. glow discharge with sample at cathode on log-log scales. The area for measurement was 0.049 cm².



0 0



Time (second)

Fig.6.44 Variation of surface potential with time for different samples, prepared with and without oxidation by glow discharge prior to selenium deposition. Two different etching process ("a" and "b") were also used. The selenium substrate temperature and thickness were 50°C and 50 µm respectively.



Fig.6.45 Log-log plot of dV/dt versus time t for samples prepared with oxide by glow discharge and without oxide. Two different etching process ("a" or "b") were used prior to oxidation.

Fig.6.46 Resistance and capacitance plotted against frequency for samples prepared by glow discharge on log-log scales. The area for measurement was 0.049 cm².

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CHAPTER 7 MAIN CONCLUSIONS AND FUTURE WORK

7.1 MAIN CONCLUSIONS

The work of this thesis clearly shows that a relatively simple piece of equipment, constructed in the laboratory, can be used to obtain interesting results on the xerographic behavior of amorphous selenium films. The most important conclusions of this study are now summarized.

The important role of the intermediate oxide layer has been demonstrated. Without 1t, dark decay is larger and the acceptance voltage from charging is smaller. It would appear that a thickness only in the approximate range of 100 to 250 Å is needed for this action, since thicker films, obtained by d.c. reactive sputtering were not as effective as the thinner ones. The action of the oxide film is not just resistive because the resistance through the film was only a fraction of that of the selenium layer. Furthermore, the acceptance voltage was dependent on the sign of the surface charge. The blocking action is therefore considered to arise from a junction effect between the oxide and

the selenium. Of the different oxidation methods tried, the most effective xerographically were d.c. glow discharge and thermal oxidation in air. In the former method, it was demonstrated that if the voltage is low and the inter-electrode spacing is large, no d.c. sputtering takes place.

In respect of the selenium film, it appears that, for a constant corona voltage, the electric field is approximately constant for different selenium layer thicknesses. This leads to an increase of acceptance voltage with selenium thickness. As might be expected, the acceptance voltage varied inversely with the dark decay rate, although of course this relationship was affected by other factors.

It was found that the residual voltage decreased with increase of selenium deposition temperature and this is attributed to a decrease in the concentration of hole traps. From the approximate quadratic increase of residual voltage with selenium thickness, the trap concentration was estimated to be about 10^{13} cm⁻³ for films deposited at 50°C. A tendency was also found for the residual voltage to decrease with decrease of selenium deposition rate.

The presence of chlorine in the selenium was quite marked. For a constant corona charging voltage, the acceptance voltage was decreased with increased chlorine content. This is a result of increased dark decay rate for a fixed acceptance voltage. The residual voltage was also reduced by the presence of the chlorine through a decrease of the trap concentration. Thus, the chlorine had opposite effects on xerographic behavior in lowering residual

voltage but increasing dark decay rate. The chlorine-doped samples also showed the two-slope behavior in plots of dV/dt versus time t on double logarithmic scales. Furthermore, the sum of the powers of t for the two slopes was near -2 on the average, which is what is predicted on the charge depletion model described in section 2.5 of chapter 2. Thus, this model would seem to apply in the chlorine-doped samples, where the chlorine evidently increases the rate of emission of holes from discrete centres in the selenium.

For the most part, the two-slope behavior was, however, not clearly apparent in the non-chlorine-doped samples. A tendency towards this behavior was seen but mainly in samples where the dark decay rate was larger. Hence, for the undoped samples, it is assumed that most of the dark voltage decay is due to injection of electrons from the aluminum substrate.

For practical xerographic use, the requirements for the photoreceptor depend on the specific application involved. However, from the present results for amorphous selenium with a thickness of about 50 micrometers, the following recommendations can be made. The selenium should be deposited at a temperature above 50°C and at a deposition rate below 1 micrometer per minute to reduce the residual voltage. The intermediate oxide film should have a thickness in the range 100 to 250 Å and be formed by either d.c. glow discharge or by thermal oxidation in air. If increased dark decay can be tolerated (eg. by using a faster printing cycle), the addition of chlorine to the selenium is helpful in further reducing the residual voltage.

7.2 FUTURE WORK

As mentioned in the introduction (chapter 1), this thesis represents only a beginning for this laboratory in the study of selenium-based materials relevant to xerographic use. Arising out of the study carried out so far, much work remains to be done. The following is a list of some of the more obvious tasks which need be carried out in future work.

(a) Measurement Process

1. The apparatus for measuring xerographic properties should be improved to incorporate an erase lamp to discharge fully the plate after each charging run, so that fatigue effects, in particular, can be conveniently determined.

2. The tungsten lamp used for illumination should be supplemented by a suitable short wavelength lamp.

3. Automation of the measuring process is needed to facilitate repetition of measurement cycles and to obtain more reproducible timing control.

4. Computer data processing would be particularly helpful to record and analyse data.

5. Additional apparatus should be set up to obtain dark current-voltage measurements through the photoreceptor films using a grid to determine potential and a sufficiently sensitive picoammeter for the current.

(b) Selenium-based Photoreceptors

(6). Samples should be studied at higher deposition temperatures (eg. 70°C), possibly with further heat treatment after deposition.

(7). Thicker selenium layers up to 500 μm should be investigated.

(8). The effect of etching prior to oxidation should be further studied.

(9). An attempt should be made to determine the actual chlorine content in the selenium films already studied in this thesis to improve the accuracy of the results.

(10). An improved procedure should be developed to prepar∍ chlorine-doped samples involving the exclusion of oxygen or air in the process. The effect of the chlorine in the selenium should then be re-studied at low selenium deposition rates.

(11). The effect of other dopants (such as phosphorus and oxygen) in the selenium should be studied.

(12). The properties of Se-Te, Se-As photoreceptor films should be investigated.

(c) Oxide Intermediate Film

(13). The d.c. glow discharge method showld be further studied using different argon-oxygen mixtures and different film thicknesses.

(14). The d.c. reactive sputtering method should be further evaluated for films prepared with thicknesses in the range 100

to 300 Å.

(15). The a.c glow discharge method should be re-evaluated with a suitable electrode arrangement.

(16). Further attempts should be made to determine aluminum oxide thicknesses by ellipsometry.

(17). Substrate metals other than aluminum but with aluminum oxide deposited by d.c. reactive sputtering should be investigated.

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Appendix The Basic Photocopying Process

The main part of this thesis has been concerned with measurements of the charging and discharging of amorphous selenium films relevant to xerographic use. However, it is of interest also to demonstrate, in a simple way, the basic photocopying process in the films made. This was done in the following way.

1. Charging

First the sample of selenium on the aluminum plate was inserted into the brass holder on the rotatable aluminum plate and located under the corotron. The selenium surface of the sample was then charged positively by switching on the high voltage d.c. supply set at 6500 volt and, as described in chapter 4, the sample was osillated back and forth underneath the corotron wire to ensure uniform charging.

2. Exposure

The charged sample was then rotated away from the corotron and a piece of white paper with typescript on it for copying,

called the original, was placed face-downwards on the sample. Then the room light was switched on for several seconds, illuminating the sample through the translucent paper.

3. Development

In darkness, the original paper was removed from the sample plate, which now contained a charge pattern of the black areas of the original. Next a mixture of toner (Xerox 1045) and carrier (Xerox 1040) was carefully poured over the selenium plate, held by hand at an inclined angle so that the powder was allowed to flow over the surface of the selenium plate by gravity. In this process the heavier carrier particles fell away but the lighter toner particles adhered to the charged parts (i.e. unexposed areas) of the selenium film surface.

4. Transfer

Next a sheet of white paper was placed over the selenium surface with its attached toner particles. The sample and paper were then rotated underneath the corotron. The back of the paper was then charged positively with the d.c. supply set to about 6 kV to transfer the toner particles to the paper. Next the sample and paper were rotated away from the corotron and the sheet of paper was lifted away from the selenium plate.

5. Fixing

The paper, which was removed from the sample and which now had attached toner particles, was held in front of a 150 watt lamp for several minutes. This heating action caused the toner to blacken the paper selectively, according to the original pattern to be copied.

Fig.A.1 shows some examples of photocopying made in this way. The quality of the copies here is of course not as good as that prepared in a commercial photocopying machine because of the very simplified method used, particularly in respect of the illumination process. However, it shows that the amorphous selenium films prepared in the laboratory are sufficient to demonstrate the xerographic photocopying process.

I. Introduction

Xerographic copying and duplicating machines are complex systems which can be divided into several general subsystems. These include the optical, photoreceptor development, transfer, and fusing or fixing subsystems. Each of these subsystems are themselves duite complex and nave been the subjects of many scientific studies. In this paper, we intend to examine the first order interaction between two of the general machine subsystems—the photoreceptor and development subsystems.

The link between the photoreceptor and development systems is the electric field in the region above the surface

I. Introduction

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I. Introduction

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Copies of originals made by commercial Xerox photocopier

Copies made by author using the simple laboratory process

Fig.A.1 Photocopies made using the simple laboratory process