

[54] **RF SPUTTERING OF TRIGONAL SELENIUM FILMS**

[75] Inventor: **Irving S. Goldstein**, Rochester, N.Y.

[73] Assignee: **Xerox Corporation**, Stamford, Conn.

[22] Filed: **Sept. 24, 1974**

[21] Appl. No.: **508,950**

[52] **U.S. Cl.** ..... **204/192; 29/572; 96/1.5**

[51] **Int. Cl.<sup>2</sup>** **C23C 15/00; H01G 9/20; G03G 5/04**

[58] **Field of Search** ..... **204/192, 298; 29/572; 96/1.5**

[56] **References Cited**

**UNITED STATES PATENTS**

|           |        |               |         |
|-----------|--------|---------------|---------|
| 1,807,056 | 5/1931 | Zworykin..... | 204/192 |
| 3,395,090 | 7/1968 | Meckel.....   | 204/192 |

**FOREIGN PATENTS OR APPLICATIONS**

|           |        |             |         |
|-----------|--------|-------------|---------|
| 1,107,451 | 1/1956 | France..... | 204/192 |
|-----------|--------|-------------|---------|

**OTHER PUBLICATIONS**

Chem. Abstr. 72, 137394n (1970).

Chem. Abstr. 72, 137399t (1970).

*Primary Examiner*—John H. Mack

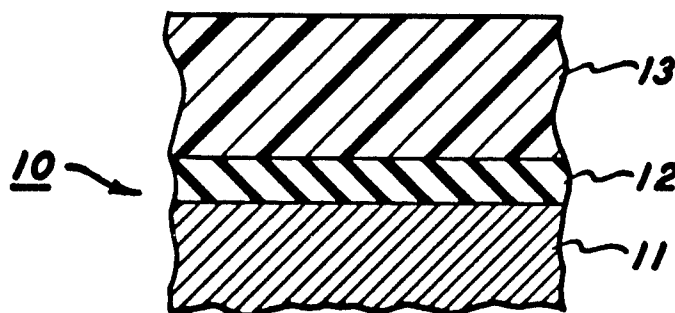
*Assistant Examiner*—Aaron Weisstuch

*Attorney, Agent, or Firm*—James J. Ralabate; James P. O'Sullivan; Jerome L. Jeffers

[57] **ABSTRACT**

Disclosed is a method of making a photoconductive imaging device which comprises directly depositing a thin layer of trigonal selenium onto a supporting conductive substrate, said deposition comprising RF sputtering said film at an RF input power of up to about 3 Watts/cm<sup>2</sup>, while producing a corresponding elemental selenium flux density of up to about 10<sup>16</sup> atoms/cm<sup>2</sup>/sec. in an Argon atmosphere maintained at a pressure of about 10 to 30 microns. The deposition is carried out onto a conductive metallic substrate maintained at a temperature in the range of about 70° to 130°C.

**6 Claims, 2 Drawing Figures**



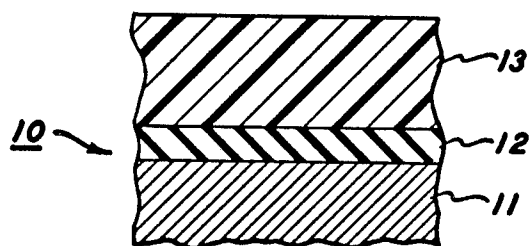


**FIG. 1**

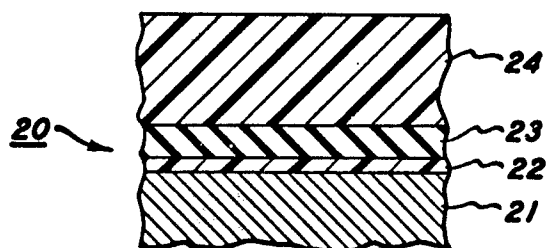


**FIG. 2**

## RF SPUTTERING OF TRIGONAL SELENIUM FILMS

### BACKGROUND OF THE INVENTION

This invention relates in general to xerography and more specifically to a method of directly depositing trigonal selenium photoconductive layers by RF sputtering.

In the art of xerography, a xerographic plate containing a photoconductive insulating layer is first uniformly electrostatically charged in the dark in order to sensitize the surface of the photoconductive layer. The plate is then exposed to an image of activating electromagnetic radiation, such as light, which selectively dissipates the charge in the illuminated areas of the photoconductive layer while leaving behind a latent electrostatic image in the non-illuminated areas. The latent electrostatic image may be developed and made visible by depositing finely divided electroscopic marking particles on the surface of the photoconductive layer. This concept was originally described by Carlson in U.S. Pat. No. 2,297,691 and is further amplified and described by many related patents in the field.

A photoconductive material which has had wide use as a reusable photoconductor in commercial xerography comprises vitreous or amorphous selenium. Although vitreous selenium has had wide acceptance for commercial use in xerography, its spectral response is limited largely to the blue-green portion of the visible spectrum (below 5200 Angstrom Units).

Selenium also exists in a crystalline form known as trigonal or hexagonal selenium which is well known to the semi-conductor art for use in the manufacture of selenium rectifiers. In the crystalline trigonal form, the structure of the selenium consists of helical chains of selenium atoms which are parallel to each other along the crystallographic c-axis. In the past, trigonal selenium was not normally used in xerography as a photoconductive layer because of its relatively high electrical conductivity in the dark, although in some instances trigonal selenium can be used in a binder configuration in which the trigonal selenium particles are dispersed in the matrix of another material such as electrically active organic material or a photoconductor such as vitreous selenium. U.S. Pat. Nos. 2,739,079 and 3,692,521, both describe photosensitive members utilizing small amounts of hexagonal (trigonal) selenium contained in a predominantly vitreous selenium matrix.

It has been found that a thin layer of trigonal selenium overcoated with a relatively thicker layer of electrically active organic material, forms a useful composite photosensitive member which exhibits improved spectral response and increased sensitivity over conventional vitreous selenium-type photoreceptors. This structure may be made by first vacuum evaporating a thin layer of vitreous selenium onto a supporting substrate followed by forming an electrically active organic layer over said vitreous selenium layer. The entire device is then heated to an elevated temperature for a time sufficient to convert the vitreous selenium to the crystalline trigonal form. This device and method are more fully described in copending U.S. pat. application, Ser. No. 473,858, directed to the Method of Fabricating Composite Trigonal Selenium Photoreceptors, and filed on May 28, 1974 (D/72448). It has been found, however, that since vitreous selenium is approx-

imately 11 percent less dense than trigonal selenium, considerable volume shrinkage occurs on converting the vitreous selenium layer to the trigonal form. This shrinkage gives rise to strains in the selenium layer and in some cases leads to cracking and pinhole formation within the resulting trigonal selenium layer. In addition, the adhesive bond between the trigonal selenium layer and the substrate can also be weakened by these strains.

### OBJECTS OF THE INVENTION

It is therefore an object of this invention to provide a method of forming trigonal selenium layers by direct deposition by RF sputtering.

It is another object of this invention to provide a method of making an imaging device containing a substantially strain-free trigonal selenium layer which exhibits good substrate adhesion.

It is a further object of this invention to provide a method for the direct deposition of trigonal selenium layers suitable for use in composite imaging members.

### SUMMARY OF THE INVENTION

The present invention is directed to the direct deposition of trigonal selenium layers by RF (radio frequency) sputtering onto heated metallic substrates. The direct deposition by RF sputtering is accomplished by using conventional-type sputtering modules in a partial pressure of an inert gas using a high purity selenium target. Sputtering under these conditions eventually results in the formation of a thin continuous polycrystalline layer of trigonal selenium which is formed on a heated metallic substrate. The trigonal selenium layer may then be overcoated with a layer of electrically active organic material, such as polyvinyl carbazole, in order to form a composite imaging device suitable for use in electrophotographic-type imaging.

One embodiment contemplated for the present invention involving the above mentioned composite device, involves uniformly charging the free surface of the active layer to a given polarity. The device is then exposed to radiation to which the electrically active transport layer is substantially non-absorbing or transparent, and to which the photoconductive trigonal selenium layer is substantially absorbing. Positive or negative electrical charges (holes or electrons) generated by the trigonal selenium layer are injected into the transport layer and moved to the surface to selectively discharge the surface charge, resulting in the formation of a latent electrostatic image which may be later developed to form a visible image.

### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates one embodiment of the imaging member suitable for using the trigonal selenium layers of the present invention.

FIG. 2 illustrates a second embodiment of an imaging member suitable for using the trigonal selenium layers of the present invention.

### DETAILED DESCRIPTION OF THE INVENTION

The process of the present invention is directed to the deposition of trigonal selenium by RF sputtering onto a heated metallic substrate. The process comprises utilizing a conventionaltype sputtering module under vacuum conditions of about  $1$  to  $3 \times 10^{-2}$  Torr. (10 to 30 microns) in an inert atmosphere such as Argon or Neon, using a high purity selenium target.

The vacuum conditions are not particularly critical and pressures outside this range may also be used. The sputtering conditions include using an RF input power of about 1 to 3 Watts/cm<sup>2</sup> with a corresponding selenium flux density of up to about 10<sup>16</sup> atoms/cm<sup>2</sup>/sec. An RF power and flux density above these maximums would tend to melt the selenium target. One critical aspect of the present invention involves controlling the substrate temperature within the range of about 70° to 130°C during the selenium deposition. In general, a film thickness of 2,000 Angstroms can be obtained on 3 inch diameter gold substrate when sputtering at 80 Watts in 10 microns of Argon at a substrate temperature of 108°C for 150 minutes. It should be understood that these conditions may all be varied somewhat in order to obtain the desired trigonal selenium morphology. In general, lower deposition rates or lower RF powers, lower the substrate temperature range for which the trigonal selenium may be obtained. Also, lower deposition rates at higher substrate temperatures in general result in larger average selenium crystallite sizes.

The trigonal selenium layers of the present invention are used in a composite imaging member suitable for use in xerographic type imaging. The figures in the drawing illustrate a suitable imaging device for such trigonal selenium layers. In FIG. 1, reference character 10 illustrates an imaging member comprising a supporting substrate 11 overlaid with a thin layer of crystalline trigonal selenium 12 which is covered with a relatively thicker layer of an organic electrically active material 13. The imaging member may be in any form such as a flat plate, drum or cylinder, drum scroll or a flexible endless belt.

The substrate 11 may be rigid or flexible and of any convenient thickness. It may also comprise a composite structure such as a thin conductive coating contained on a dielectric base.

The substrate 11 must be made up of a suitable conductive material. Several substrate properties appear to be of importance for use in the present invention. First, the substrate must be electrically blocking with respect to trigonal selenium. Alternatively, the substrate could be covered with a thin blocking layer to prevent charge injection from a non-blocking substrate into the trigonal selenium layer. Second, the number of heterogeneous nucleation centers for trigonal selenium growth is very important. Nucleation centers of this type are normally found on the surfaces of most substrates. While it is important that the substrate contains a sufficient number of nucleation sites for trigonal selenium formation and growth, there is reason to believe that an excessive number of nucleation sites can give rise to a form of trigonal selenium which is too conductive in the dark to be of xerographic utility. This phenomenon may be related to the size of the selenium crystallites since the crystallite size can be dependent upon the density of nucleation sites on the substrate surface. Hence, the density of nucleation sites on the substrate is very important. The number of these sites depends on the nature of the particular substrate being used and must be determined empirically. Third, it is important that the substrate-vapor surface tension,  $\gamma_{s-v}$ , be kept as high as possible and that the substrate-selenium interfacial tension,  $\gamma_{s-se}$ , be kept as low as possible. Since  $\gamma_{s-v}$  and  $\gamma_{s-se}$  are inherent properties of the substrate and selenium, optimization of these can best be achieved by careful substrate selection. Gold was first

used as the substrate material since it has a relatively high surface-free energy and does not appreciably oxidize. Anodized aluminum was used since it is known to have a low electronic work function and thus does not inject into trigonal selenium. It was concluded that a preferred group of suitable substrate materials would be those having high surface energies and low electronic work functions including such metals as tantalum, zirconium, titanium and zinc. By thus optimizing these parameters, imaging members can be produced with suitable xerographic properties. The increased ability of sputtering to produce trigonal selenium over evaporation techniques is due to the increased surface mobility of the selenium during sputtering. This increased surface mobility is due to the higher kinetic energy, the heating plasma and the high critical nucleation temperature associated with RF sputtering. Therefore, with regard to the substrate, any suitable conductive material taking into account the above criteria may be used in the present invention.

Trigonal selenium layer 12 is formed by the techniques already described above and must be maintained in a critical thickness range of about 0.03 to 0.8 microns (300 to 8000 Angstroms) in order for the device to function effectively. Thicknesses below about 0.03 microns do not absorb sufficient amounts of light and, therefore, do not generate sufficient numbers of electrical charges, while thicknesses above about 0.8 microns result in an excessively high dark conductivity and the plate will not function adequately to be useful for imaging.

In general, the active layer 13 may comprise any suitable transparent organic polymer or nonpolymeric material capable of supporting the injection of photoexcited holes from the photoconductive layer and allowing the transport of these holes through the organic layer to selectively discharge a surface charge. Typical polymers include poly-n-vinylcarbazole (PVK), poly-1-vinylpyrene (PVP), poly-9-vinylanthracene and others. Typical nonpolymeric materials include carbazole, pyrene, tetraphenyl pyrene, benzochrysene, perylene, tetracene, pycene, fluorene, fluorenone and naphthalene. A larger group of suitable materials for use in layer 13 are more fully described in copending application Ser. No. 371,647, filed on June 20, 1973, which are incorporated herein by reference.

Alternatively, an electron transport material may also be used for layer 13. A typical electron transport material comprises 2,4,7-trinitro-9-fluorenone (TNF). The TNF may be used alone or in combination with relatively electrically inactive organic materials such as polyesters or complexed with other active materials such as polyvinyl carbazole.

In general, the thickness of the active layer should be from about 5 to 100 microns, but thicknesses outside this range can also be used.

In imaging the above device, the free surface of the active material is uniformly electrostatically charged to a given potential. The device is then exposed to a pattern of activating radiation of a wavelength such that the layer 13 is substantially nonabsorbing or transparent to the imaging light. This light generates electron-hole pairs in photogenerating layer 12 and for hole transport materials, positive charges or holes are injected into and transported through active layer 13 to selectively discharge a surface charge which results in the formation of a latent electrostatic image. This image may then be developed in any conventional man-

ner to form a visible image.

It is not the intent of this invention to restrict the choice of active materials to those which are transparent in the entire visible region. For example, when used with a transparent substrate, imagewise exposure may be accomplished through the substrate without the light passing through the layer of active material. In this case, the active material need not be nonabsorbing in the wavelength region of use.

Another modification of the layered configuration is illustrated in FIG. 2 and optionally includes the use of a blocking layer at the substrate-photoconductor interface. This configuration is illustrated by photosensitive member 20 in which the substrate 21, and trigonal selenium photoconductive layer 23 are separated by a blocking layer 22. Active transport layer 24 overlays photoconductive layer 23. The blocking layer functions to prevent the injection of charge carriers from the substrate into the photoconductive layer. Any suitable blocking material which meets the above criteria for the substrate may be used.

It is preferred that trigonal selenium photoconductor and the active organic material should be selected or matched to provide that the active layer be nonabsorbing to light in the wavelength region used to generate photoexcited carriers in the photoconductive layer for carrier injection into the active organic layer. This preferred region of xerographic utility is from about 4000 to 7000 Angstrom Units. In addition, the trigonal selenium being responsive to most wavelengths from 4000 to 7000 Angstrom Units is suitable for a panchromatic response.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples further specifically define the present invention with respect to a method of making a photosensitive member containing a photoconductive layer of trigonal selenium. The percentages are by weight unless otherwise indicated. The examples below are intended to illustrate various preferred embodiments of the present invention.

#### EXAMPLE I

The direct deposition by RF sputtering of a continuous trigonal selenium film is carried out using a modified Materials Research Corporation Model 8620 sputtering module on a Welch 3102 turbomolecular pump. A flat temperature controlled substrate holder is placed opposite and parallel to a hot pressed 7.62 cm diameter high purity selenium target (99.99% purity) which is epoxy bonded to a copper backing plate. In the standard sputtering module the substrate holder was substituted for one of the upper sputtering targets and the selenium target was put on the lower target holder with the spacing between the target and substrate set at 6.35 cm. The selenium is sputtered onto a 5 cm by 5 cm gold coated aluminum plate. The ranges of sputtering conditions which resulted in trigonal selenium film are:

|                               |                                |
|-------------------------------|--------------------------------|
| Net RF input power            | : 40-105 Watts                 |
| Corresponding to a Se flux of | : $1.28 - 6.57 \times 10^{14}$ |
|                               | : atoms/cm <sup>2</sup> /sec   |
| Argon gas pressure            | : 10 - 30 microns              |
| Substrate temperature         | : 80 - 120°C                   |

Two examples of sputtering runs which resulted in continuous trigonal selenium films of a few thousand Angstroms thickness can be given. The first film was

sputtered at 80 Watts in 10 microns of Argon at a substrate temperature of 108°C for 150 minutes. The second film was sputtered at 85 Watts in 10 microns of Argon at a substrate temperature of 98°C for 60 minutes. In general, lower deposition rates (lower RF powers) lowered the substrate temperature range for which trigonal selenium could be obtained. Lower deposition rates at higher substrate temperatures, in general, resulted in larger average selenium crystalline sizes. Due to the injecting property of the gold substrate, these films could not be tested xerographically.

#### EXAMPLE II

A trigonal selenium layer is formed over an anodized aluminum substrate by the method set forth in Example I. A 12 micron layer of polyvinyl carbazole is then formed over the trigonal selenium layer by draw bar coating from a solution of polyvinyl carbazole. This composite device is capable of being imaged in a xerographic manner to form a visible image.

Although specific components and proportions have been stated in the above description of the preferred embodiments of the present invention, other modifications and ramifications of the present invention would appear to those skilled in the art upon reading the disclosure. These also are intended to be covered in the scope of this invention.

What is claimed is:

1. A method of making a photoconductive imaging device which comprises:

directly depositing a thin layer of trigonal selenium onto a supporting conductive substrate, said deposition comprising RF sputtering said film at an RF input power of up to about 1 to 3 Watts/cm<sup>2</sup> while maintaining a corresponding elemental selenium flux density up to about  $10^{16}$  atoms/cm<sup>2</sup>/sec. in an inert atmosphere under vacuum conditions, said deposition being carried out while maintaining the conductive substrate at a temperature in the range of about 70° to 130°C, said substrate being of a material which is electrically blocking with respect to trigonal selenium or is covered with a thin electrically blocking layer to prevent charge injection and which has an adequate number of heterogeneous nucleation centers for trigonal selenium growth but not so many sites so that the process gives rise to a form of trigonal selenium which is too conductive in the dark to be of xerographic utility and such material having a sufficiently high substrate-vapor tension and a sufficiently low substrate-selenium interfacial tension to permit the effective application of the trigonal selenium to its surface by RF sputtering.

2. The method of claim 1 in which the substrate comprises anodized aluminum.

3. The method of claim 1 in which a layer of electrically active organic material is then formed over the trigonal selenium layer.

4. The method of claim 1 in which the electrically active layer comprises a material selected from the group consisting of polyvinyl carbazole, polyvinyl pyrene, 2,4,7-trinitro-9-fluorenone, and mixtures thereof.

5. The method of claim 3 in which the thickness of the deposited trigonal selenium layer is from about 300 to 8000 Angstrom Units.

6. The method of claim 1 in which the substrate comprises a metal selected from the group consisting of tantalum, zirconium, titanium and zinc.

\* \* \* \* \*