CONDUCTIVITY INDUCED BY CATHODE RAYS IN CADMIUM-SELENIDE LAYERS

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Summary
Measurements were carried out on the conductivity induced by electron irradiation of cadmium-selenide layers. The layers were prepared by evaporation of cadmium selenide while afterwards an amount of $10^{-3}$ Cu was evaporated onto the layer in order to activate it. The gain of the induced current with respect to the primary current of the electron beam was determined as a function of the voltage applied to the layer for 10-kV, 15-kV and 20-kV electrons; a gain of more than 2000 was found. Further the dependence of the gain on the primary current and the decay of the induced current were measured, the latter being 0.25 msec.

Résumé
La conduction induite par rayonnement cathodique a été mesurée pour des couches de sélénium de cadmium. Les couches ont été préparées par évaporation du sélénium de cadmium, après cela une quantité de $10^{-3}$ Cu a été évaporée pour activation. L’amplification du courant induit en proportion du courant primaire a été déterminée comme fonction de la tension de la couche pour des électrons avec des tensions de 10 kV, 15 kV et 20 kV, une amplification de plus de 2000 était obtenue. De plus la dépendance de l’amplification du courant primaire et le temps de déclin ont été mesurés, le dernier étant 0,25 msec.

Zusammenfassung
Es wurde die von Elektronenbestrahlung induzierte Leitfähigkeit von Kadmiumselenid-Schichten gemessen. Diese Schichten wurden hergestellt durch Verdampfung des Kadmiumselenids, nachher wurde zur Aktivierung $10^{-3}$ Cu verdampft. Die Verstärkung des induzierten Stroms im Verhältnis zu dem primären Elektronenstrom wurde bestimmt als Funktion der Spannung der Schicht für 10 kV, 15 kV und 20 kV Elektronen; eine Verstärkung von mehr als 2000 wurde erreicht. Weiter wurden die Abhängigkeit der Verstärkung des primären Stroms und die Abklingungszeit gemessen, die letztere war 0,25 msec.

1. Introduction
In many cases the conductivity of a layer of a semiconducting or insulating material increases considerably when it is irradiated by a cathode-ray beam. The current $i_\alpha$ produced by an electric field between electrodes applied to the layer may increase by an amount $\Delta i_\alpha$ due to the irradiation and which is much greater than the primary current $i_\alpha$ of the cathode-ray beam. This amplification is defined as $g = \Delta i_\alpha/i_\alpha$. Many materials showing this effect $^1$, which is sometimes called “bombardment-induced conductivity” (B.I.C.), are already known $^1$, e.g. Al$_2$O$_3$, CdS, Ge, Si, Se, Sb$_2$S$_3$.

We have carried out some measurements on evaporated cadmium-selenide layers. The purpose of our experiments was to find out whether, in view of
their efficiency and decay, these layers were suitable for use as a target in a television-camera tube. Here light from a scene strikes a photocathode; the emitted electrons are accelerated and impinge on the B.I.C. layer. The amplified current is used as the video signal. Normally one side of the B.I.C. layer has a conducting layer. The potential of the other side is stabilized by scanning the layer with a focused beam of electrons.

Figure 1a represents an arrangement for irradiating and scanning the same side of the layer, fig. 1b that for irradiating one side and scanning the other. In the latter case the layer must be either self-supporting or supported by, for example, a fine-mesh grid. The requirements for this layer are similar to those for the vidicon, in which the layer is directly irradiated by the light of the scene. These requirements have been discussed by Heyne. The main points are that

![Diagram of Fig. 1a](image)

**Fig. 1. a.** Schematic arrangement for irradiating and scanning the same side of the layer.

![Diagram of Fig. 1b](image)

**Fig. 1. b.** Schematic arrangement for irradiation of one side and scanning of the opposite side of the layer.
the thickness of the layer should lie between 5 and 25 \( \mu \) (corresponding to a capacity of between 800 and 4000 pF for an area of about 2 cm\(^2\)) and that the specific resistance of the layer should be very high, viz. some \( 10^{12} \Omega \text{cm} \), although often the total resistance will depend also on the type of the contacts. Further the decay time of the induced current should be smaller than about 0.04 sec, the time in which a complete raster is described on the target (i.e. the current should have decreased to but a few per cent in 0.04 sec).

To get a signal-to-noise ratio of at least 10, it is necessary for 100 electrons to fall on every element of the target during each scanning cycle. Because a single element is scanned in about \( 10^{-7} \) sec (625 \& 625 elements should be scanned in 0.04 sec), the total current should be \( 10^9 \) electrons per second corresponding to \( 1.6 \cdot 10^{-10} \) A.

If an amplification of only about 100 times is obtained, then the photon noise of the induced current becomes of the same order as the noise of a good video amplifier (about \( 10^{-8} \) A). This low amplification would have the advantage of being sufficient for using the electrons excited by the primary cathode-ray beam in the layer. There would therefore be no need for a replenishment of electrons by the electrodes, which can give rise to long decay times.

2. Preparation of the layers

The starting material used was a very fine electronic-grade CdSe powder, obtained from Merck, Rahway, N.Y., U.S.A. We fired this powder at 1000 °C in a stream of pure nitrogen for one hour in order to remove all volatile material absorbed by the powder. The firing treatment caused the fine and loose powder to shrink and sinter to coarse polycrystalline lumps of cadmium selenide. The evaporation of the cadmium selenide was carried out from a molybdenum crucible with a heating spiral of tungsten wire cemented into the bottom of it. A charge of 2.0 g could be evaporated in about 45 min. In order to activate the evaporated layer of CdSe, a certain amount of Cu was evaporated onto it from a small platinum loop directly after the evaporation of the CdSe. The desired amount of copper was applied to the Pt wire by electrolysis and could thus be dosed easily and exactly. We obtained the best results with about \( 10^{-3} \) gram atoms Cu per gram molecule of CdSe. The evaporation crucible and Pt wire were both mounted on a revolving support, and thus the two materials could be evaporated from the same place 11 cm below the substrate. The pressure in the evaporation chamber was always kept between \( 10^{-6} \) and \( 5 \cdot 10^{-6} \) mm of mercury during the evaporation of both materials.

The substrate was lime glass covered on one side with a layer of conducting tin oxide, the cadmium selenide being applied to the conducting side of the glass plates. In order to obtain a thick layer (10-15 \( \mu \)) adhering well to the substrate, we had to heat the glass plates to about 150 °C during the evaporation
of the CdSe layer. The temperature of the glass plates was controlled by a stainless-steel block equipped with heating wires and a thermocouple. The temperature of the block was measured continuously during the whole evaporation procedure. A reproducible heat exchange between block and glass plates was obtained by leaving a gap of 1 mm between the block and the upper glass surface, so that the only heat transfer was caused by radiation. Before the evaporation the glass substrate was heated to 300-400 °C in order to desorb water from the surface. After the evaporation of both materials, the glass slides now bearing a CdSe layer were allowed to cool down to about 80 °C in 2 hours before air was admitted to the evaporation chamber.

The temperature of the substrate during the evaporation has an influence upon the structure of the evaporated layer. The higher the temperature, the more chance the condensing material has to arrange itself as a neatly crystallized solid. Besides, the temperature of the substrate will influence the stoichiometry of the solid since the CdSe very probably volatilizes as Cd and Se atoms. Heating to about 150 °C of the substrate was found to lead to a good adhesion of the CdSe layer.

The CdSe (Cu) layers prepared in this manner did not yet exhibit good B.I.C. properties because of high dark conductivity. The large conductivity of evaporated layers of CdSe and also CdS is thought to be caused by the large excess of Cd in the layers, which can be formed under certain evaporation conditions (part of the excess Cd, occurring as free cadmium, renders the colour of an evaporated CdS layer from orange to black). Such an excess of Cd can be removed by heating in vacuum, in hydrogen sulphide or selenide or in sulphur or selenium vapour.

We chose an aftertreatment in sulphur and selenium vapour for the following reasons. Conducting tin oxide could stand heating in sulphur and selenium atmosphere up to 450 °C (hydrogen sulphide reduces tin oxide at much lower temperatures). Not only will the free Cd excess react in S or Se vapour, but also the Cd excess built into the CdSe lattice (interstitial Cd or Se vacancies) probably causing n-type conduction, will be reduced by the aftertreatment 4).

The vapour pressure of Se at 450 °C is still very low and the dark conductivity of the cadmium-selenide layers did not decrease to a value sufficient for our purpose. The saturation pressure of sulphur at 450 °C is already 1 atmosphere. However, we used a pressure of 5 cm of mercury and fired the layers at 350-420 °C in the apparatus shown in fig. 5. Sulphur boiling in the lower furnace sent up its vapour through the heating zone in the upper furnace and condensed on the glass wall above the second furnace. The condensed sulphur was allowed to flow back through the parallel tube insulated with asbestos cord.

Before the heating, the tube, already with the layers in it, was flushed with nitrogen a few times, and after that connected to a pressure regulator and a rotary vacuum pump. During this treatment the copper could also react with
the sulphur and diffuse into the cadmium-selenide layer. At higher temperatures, and firing times of several hours, an appreciable amount of the CdSe changed to CdS.

Aluminium electrodes were applied in vacuum after the heat treatment in sulphur vapour (fig. 2).

![Circuit Diagram](image)

Fig. 2. Circuit diagram. $a =$ Al-layer thickness 0.1 $\mu$; $b =$ tin-oxide layer.

3. Measurements

The experiments were carried out in a demountable cathode-ray tube, described elsewhere \(^3\). In most experiments the surface of the cadmium-selenide layer was covered by a thin layer ($\approx$ 0.1 $\mu$) of aluminium. Thus the cadmium-selenide layer was sandwiched between two conducting layers (see fig. 2), the tin-oxide layer $b$ and the thin aluminium layer $a$. The electron beam passes through this thin aluminium layer into the cadmium selenide, which had a thickness of about 15 $\mu$.

A d.c. voltage $V_s$ was applied to the electrodes of the cadmium-selenide layer. The current $i_s$ in the cell circuit was measured under steady irradiation by the primary electron beam (voltage $V_p$, current $i_p$). Amplification was only found if the polarity of $V_s$ was such that the irradiated side of the layer was negative. This may be due to the fact that in cadmium selenide only the electrons possess good mobility.

The highest energy of the electrons of the primary cathode-ray beam was 20 kV, so that the electrons had a penetration depth of about 2 $\mu$, which was far less than the layer thickness of about 15 $\mu$. Therefore the secondary electrons were formed in a layer of about 2 $\mu$ near the surface. When the polarity of the surface was negative with respect to the tin-oxide layer, the electrons were transported by the field through the cadmium selenide to the tin-oxide electrode.

However, when the surface was positive, no steady current was possible because the holes are immobile. Amplification with this polarity of the surface would be possible only if the layer thickness was equal to (or smaller than) the penetration depth of the primary electrons.
Fig. 3. Gain as a function of voltage $V_s$ for two layers.

The results of the measurements for two layers ($a$ and $b$) are given in fig. 3, where $g$ is plotted as a function of $V_s$. For layer $a$ the specific dark resistance was about $10^{11} \, \Omega \cdot cm$, the gain increased very progressively with $V_s$, being almost proportional to the square of $V_s$. This might indicate the formation of a space charge in the non-irradiated interior of the layer $^5)$. Thus the current in the layer will be space-charge limited, giving theoretically a superlinear law for the relationship between $g$ and $V_s$.

Because steady irradiation was used and no saturation of the gain with increasing $V_s$ was found, it seems that replenishment of the electrons by the cathode must be present. Sometimes a much lower dark resistance was found, for instance for layer $b$, having a specific dark resistance of about $4 \times 10^9 \, \Omega \cdot cm$. In these cases the induced current was about equal to the dark current. Then there will be no appreciable influence of the space charge on the induced current. Thus a nearly linear increase of $g$ with $V_s$ was found.

For layer $a$ curves are given with the primary voltages $V_p = 10 \, kV$, $15 \, kV$, and $20 \, kV$. The slopes of the lines are not the same for different voltages. This is not quite understood but may be due to inhomogeneous activation of the layer or to the presence of barriers near the electrodes.

In fig. 4 the gain is shown as a function of the primary current $i_p$. The gain decreases strongly as $i_p$ increases. This will be caused by a higher probability...
Fig. 4. Gain $g$ as a function of the primary current $i_p$.

Fig. 5. Apparatus for the heat treatment of the layers in a sulphur atmosphere.

of direct recombination of the electrons and the holes at high excitation densities.

The decay time of the conductivity was measured by interrupting the electron beam periodically. Rectangular voltage pulses, at a frequency which could be varied, were fed to the grid of the cathode-ray tube. The photocurrent was recorded by an oscilloscope with d.c. amplification, so that the line of zero output was always known. It was shown that the intensity had fallen to its
halfvalue in 0·25 msec while less than 3% of the initial intensity is left after 20 msec.

Acknowledgement
We are indebted to Mr. Th. J. Westerhof for his assistance in carrying out the measurements.

Eindhoven, April 1962

REFERENCES

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