A new Leddicon target sensitive in the 1000-2000nm waveband and beyond

by G.P. Hopkins and D.G. Swain

1. INTRODUCTION

There are numerous requirements for inexpensive TV imaging systems to cover the near infra red spectrum out to 2000nm. Applications include covert surveillance, semiconductor inspection, laser and thermal imaging. At the heart of such a system is the image pick-up device: usually in the form of a vacuum tube of the Vidicon type or a solid state sensor array.

Unfortunately there are very few photoemissive or photoconductive materials that can be employed as sensors for cameras across the 1000-2000nm band. Image tubes using the S1 (Ag/O/Cs) photocathode work to 1500nm but have poor sensitivity. Most silicon devices in the form of Vidicon targets or CCDs are not sensitive beyond 1100nm. Only the PtSi Shottky barrier imagers cover this spectrum, but they are expensive and require cooling to reduce dark currents to tolerable levels.

For over 50 years lead sulphide has been used to detect near infra red radiation to its limit of 3300nm, but because of its low resistivity $(10^{-10} \, 0^$

In 1949 Frank and Raithel (1) compromised by combining PbO and PbS in the hope of making a more viable IR photoconductive target. Their method was to evaporate first a PbO film and then subject it to sulphur vapour at elevated temperature followed by further heat treatments. Although the spectral response they obtained extended from the visible to about 1800nm the sensitivity was non uniform, dark currents were high and the image retention was severe.

Later work by Heimann and Kunze (2) and Hori et. al. (3) claimed to improve the transient response or lag, but picture qualities still were deemed to be very poor. More recent developments by Kawai et.al. (4) extended the spectral limit of their Vidicon to 2700nm by using a very lengthy version of the original Frank and Raithel process. There remained however many practical problems concerned with reproducibility in the production process and the stability of target and tube performance.

R Registered Trade Mark of EEV Co. for photoconductive camera tubes with lead oxide targets.

To meet the market demand for near IR imaging we utilised Leddicon technology to develop a new PbO/PbS photoconductive target for 18mm and 25mm diameter tubes. Depending on the ratio of oxygen to sulphur the spectral response can be optimised in the 1000-2000nm waveband, while still being sensitive to visible light. Target cooling is not needed and the tubes can be mounted in the cheapest single tube Vidicon cameras fitted with standard lenses. Two tube sizes 18mm and 25mm are currently available commercially as the XQ1610 and XQ1615 series infrared Leddicons (5).

In this paper we show how the spectral sensitivity and other target characteristics such as lag and resolution are influenced by the layer processing parameters and tube operating conditions. Target performance is further illustrated by some of the tube and camera applications.

2. TARGET PROCESSING

In a previous paper Hopkins (6) reviewed the materials and processes used for manufacturing lead oxide targets. It was shown how the addition of a small amount of sulphur to the evaporated PbO layer shifts the long wavelength cut-off from 650nm to 750nm to effect a more natural colour balance in colour television. The more extensive spectral response of the infra-red Leddicon target shown in Fig.(1) was developed along similar lines but uses larger quantities of sulphur.

Target processing can be divided into four sequential stages:

- 1) Evaporation of the PbO layer
- 2) Sulphurisation
- 3) Blocking contact formation
- 4) Tube conditioning.

2.1. Evaporation of the Lead Oxide layer

The starting point is the PbO layer which is evaporated from PbO granules in a platinum boat through a gas ambient $(10^{-3} - 10^{-4} \text{ torr})$ of oxygen and water vapour onto a glass window previously coated with a transparent but conducting layer of tin oxide or indium tin oxide. Fig. 2 is an SEM picture of a typical PbO layer 8000nm thick. It comprises a large number of individual PbO crystallines (or platelets) of dimensions no more than 1000 x 100 x 10nm. The crystalline structure is of the tetragonal form (litharge) and the preferred orientation is for (110) planes parallel to the faceplate surface. This is shown more explicitly in the schematic Fig. 3. For imaging purposes this configuration allows the right capacitance for charge storage and ensures a high conductivity through the thin layer while minimising the conductivity across the layer.

Lead oxide is an amphoteric semiconductor whose conductivity type is determined by the ratio of lead to oxygen in the crystalline lattice (e.g. an excess of oxygen causes p-type conductivity).

If the PbO were evaporated in vacuum then because of preferential loss of oxygen by dissociation the layer would be degenerate n-type. To compensate a partial pressure of oxygen is added during evaporation together with a partial pressure of water vapour to achieve finer control over the conductivity. In preparation for an infra-red target the PbO conductivity is usually made slightly n-type.

The size, orientation and packing density of the crystallites depends on the conditions of deposition. Here the faceplate temperature and evaporation rate are the main parameters which are controlled by the ambient gas partial pressures, boat temperature and evaporation geometry (Fig. 4). Lead oxide evaporated from the boat has a heat of condensation too high for the desired layer growth so it is necessary to fix the faceplate temperature using a regulated heat sink. Excessively high faceplate temperatures (greater than 150°C.) tend to encourage large crystallite growth which can result in a grainy texture to the image. While higher boat temperatures increase the evaporation rate, a higher gas pressure tends to slow it down. This is because the gas acts as an impedance, thus scattering the evaporating flux of PbO and dissociated components, and changing the dynamics of the layer growth. Pressures higher than 10^{-3} torr generate a very porous layer with a "fluffy" texture. This is undesirable if variations in texture across the surface of the target cause shading patterns on picture.

Geometrical dimensions like boat to faceplate distance, boat aperture and angle of evaporation are all optimised to achieve near uniform layer thickness and minimum sensitivity variation across the target.

2.2. Sulphurisation

Large numbers of small PbO crystallites present a very high effective surface area, typically 5-10m² for a layer of 25mm diameter, onto which gas may adsorb. A convenient method of introducing sulphur therefore is by adsorption. Unlike previous workers (3) who evaporated PbS or exposed to sulphur vapour at elevated temperature (4) we prefer to dope PbO using hydrogen sulphide, H₂S. This is relatively easy to control in small quantities and can be made to permeate the whole layer structure. Then as the layer temperture is raised the adsorbed H₂S reacts according to:

 $PbO + H_2S \rightarrow PbS + H_2O$.

Following thermal desorption of H_2O , the PbO crystallites are left with a "skin" of PbS. Xray diffraction shows the PbS has random orientation. Coincidentally the layer changes colour from yellow/orange to brown/black and the absorption edge shifts as shown typically in Fig. 5. The extent of this shift (narrowing bandgap energy) and the consequential change in spectral response depends on how much H_2S is introduced and the length of the heat treatment. Overall the sulphurisation process takes only a few minutes.

2.3. Blocking Contact Formation

For the target to operate in the normal scanning mode with the minimum of dark current it is necessary to block injection of holes from the front signal contact and electrons from the rear scanning beam. Hole blocking is provided adequately by a potential barrier at the tin oxide - lead oxide interface. Electron blocking however is not so easily provided and necessitates a further stage of processing after sulphurisation.

A system of electron traps is laid down on the back surface of the target by bombarding with oxygen ions from a glow discharge. These traps when fully charged negatively, repel further electrons from the scanning beam. The blocking action is broken only temporarily when positive image charge is neutralised (i.e. when signal current flows) or if an excessive target voltage is applied.

The implanted oxygen ions probably form higher oxides of lead in a very thin layer which is stable chemically and ensures a good operating life for the target.

2.4. Tube Conditioning

After the target is mounted into the tube there follows a number of process stages aimed at conditioning the tube to its operating specification. Initially the cathode is activated and the tube is degassed to attain a vacuum of 10^{-0} torr before the getters are fired and the tube is sealed off. Further loosely bound gas is removed by scanning the tube for a few days while illuminating the target with broadband light. Surplus oxygen in particular is "scanned out" of the target to be taken up by the getter. Many unwanted charge trapping centres are thereby eliminated so that target sensitivity, resolution and transient response are maximised.

3. TARGET PERFORMANCE

3.1. Spectral Response

Figure 6 shows the spectral response for one 18mm and two 25mm diameter tubes in the 1000-2000nm waveband. Visible light is filtered out by a Hoya RM100 filter which is responsible for the fall off below 1100nm. The XQ1610 and XQ1610-07 targets have identical layer thickness, but the latter type was processed with extra stages of sulphurisation (S content approximately 15% by weight) to extend the spectral response which cuts off beyond 2200nm. The response for the XQ1615 differs from the XQ1610 because of different layer thickness and conditioning requirements for the smaller diameter tube.

3.2. Sensitivity and Dark Current

For a given absorbancy to infrared light, the sensitivity of a target is strongly influenced by the internal electric field which in turn is determined by layer thickness, trapped charge distribution and applied target voltage. Fig. 7 shows how the integrated signal varies with target voltage for two 25mm targets.

For the XQ1610 there is a steady rise in signal with increasing gradient beyond a certain voltage where the dark current also begins to rise rapidly. At lower voltages the almost flat level of dark current indicates good blocking of the scanning electron beam; but at higher voltages the blocking barrier is broken down and beam injection occurs. Normal operation would be in the blocking region with a dark current of 5-10nA. If higher sensitivities are required then the target voltage may be increased but dark currents should not exceed 20nA for long periods.

For the XQ1610-07 the signal increases more rapidly with target voltage and the dark current rises sooner. A dark current value of 40nA can be tolerated.

There are good reasons for limiting the dark current and sensitivity. If the target voltage is set too high there can develop a non uniform dark current over the target area. This usually occurs around the edges first where the layer is slightly thinner, and the picture begins to take on a grainy appearance. A variation in sensitivity, or shading, results which is sometimes difficult to correct electroniclly. The best quality targets are selected for minimal shading, typically 10-15% with a maximum 30%, while lower quality grades can be used in applications where shading is less important.

Temperature is the other factor affecting dark current and it is essential that in camera temperatures (often 6-10°C above room temperature) should be stabilised before doing quantitative work. Targets with extended spectral response are especially prone to temperature drift. Continuous running at temperatures above 40°C. will limit the useful life of the tubes.

3.3. Light Transfer Characteristic

Fig. 8 shows the light transfer characteristics for two typical examples of the XQ1610 and XQ1610-07. The slope of these curves, or δ , is usually 0.6-0.8 tending to fall at high illumination levels. This is sufficient for most applications. Values of δ vary from tube to tube and depend slightly on operating target voltage.

3.4. Amplitude Response

Good resolving capability depends on efficient infrared absorption with minimum scattering, a high electric field through the target and little leakage of image charge across the target back surface. Other factors like tube geometry, the camera and optical system also affect resolution.

Fig. 9 shows a typical amplitude response for three tube types. The XQ1610 will resolve at least 25% at 400TVL but 30-35% is more typical. Higher values of 40-45% can be achieved by adjusting process parameters to limit the spectral response. The XQ 1610-07 does not resolve quite as well mainly because of the lower operating target voltage and slightly higher lateral charge leakage. The smaller XQ1615 resolves least well because of tube geometrical factors.

3.5. Transient Response

The infrared Leddicon is an inherently laggy device compared to its counterpart in colour broadcast television. The extra charge trapping centres created by sulphurisation cause a photoconductive lag which dominates the transient response. Any beam discharge lag is small.

Fig. 10 shows the typical decay lag characteristics for the three tubes. After 3 or 4 fields the signal falls to 50% of peak but beyond this targets with the widest spectral response have the worst lag. For many applications high lag can be tolerated, but for covert surveillance work it cannot. Much faster response is attained however if smaller quantities of sulphur are used to limit the spectral cut-off at 1200nm.

4. APPLICATIONS

4.1. Thermal Imaging

Any objects above 150° C irradiate enough infrared to be detected and imaged by an infrared Leddicon. One simple example is that of a hot soldering iron as shown in Fig. 11. With a proper calibration it is possible to detect temperature differentials of 5°C. The XQ1610-07 is probably the best tube for this application.

One very popular application is for monitoring thermal leaks in large boilers and cement kilns using remote but relatively inexpensive cameras that can be left running continuously. Similar cameras are used in the quality control of welding operations and for sensing the temperature of hot extruded steel before cutting and forming. Another simple example is the safety inspection of flames such as hydrogen which burns with almost no colour. Fig. 12 shows photographs of a hydrogen furnace. The pilot light is the only visible indicator that the hydrogen is burning but in the broad infrared the flame is very conspicuous. There are more applications of this type in the gas, chemical and aerospace industries.

4.2. Surveillance

Active night vision is possible with tubes specially selected for low lag. The infrared Leddicon offers particular security advantages since long wavelength illumination can be used outside the 1100nm sensing limit of silicon imaging systems. Tests have shown that faces are easily recognisable under illumination from a bank of infrared LEDs.

Other surveillance applications include dark room observations especially in film processing laboratories.

4.3. Semiconductor and Thin Film Studies

Most semiconductor materials are transparent to infrared in the 1000-2000nm waveband. An infrared Leddicon camera mounted on a microscope can be used to examine the infrared transmitted through materials and image features such as metallic contacts and multi layer structures. If closely spaced filters are used then different impurity levels in the bandgap can be distinguished through subtle changes in transmittance.

It is also possible to view the light emitted from infrared LEDs and solid state lasers for non destructive quality control tests during fabrication.

Many materials exhibit birefringence when stressed by lattice defects. Such defects appear enhanced when viewed in transmitted polarised light as the plane of polarisation is rotated. Some examples are seen in Fig. 13.

4.4. Fibre Optic Transmission

With the increasing use of lasers at 1300 and 1550nm in fibre optic telecommunications it is important to be able to analyse the fibre optic core and cladding materials. By illuminating one end of a fibre and imaging the interference pattern with an infrared Leddicon camera at the other end, the refractive index of the material can be deduced.

4.5. Inspection of Documents and Artworks

Inks and pigments from different manufacturers which appear on reflection to have similar visible colouring, can be very different in the infrared from 650-2000nm. An example of this is shown in Fig. 14 where an attempted forgery of a bank cheque, using black ball point ink, has been detected by an infrared Leddicon camera.

Picture restorers find infrared imaging by reflection useful for "seeing through" layers of dirt and grime on paintings. This technique can be helpful also in checking the authenticity of artworks of various types.

5. Future Developments

There are areas where we wish to improve the performance of the infrared Leddicon target. Higher sensitivity and a further extension of the spectral response are desirable, but without compromising the shading, lag or resolution. To achieve this the infrared absorbancy of the target must be improved while losses by transmission and reflection in the optical system are minimised. Of particular concern is the optical transparency of the tin oxide/indium tin oxide conducting coating, which falls considerably at longer wavelengths. We are currently looking for alternative materials.

Finally, we believe there are applications for the infrared Leddicon in areas which have not been fully investigated. Examples might be in the medical fields of laser surgery and opthalmic diagnosis.

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References

- 1. K. Frank and K. Raithel. Z. Phys. Vol. 126 p377 1949.
- 2. W. Heiman, C. Kunze Infra Red Physics Vol 2 p175 1962.
- 3. H. Hori, S. Tsuji and Y Kinchi. Television Vol.21 p477 (1967).
- 4. T. Kawai, K. Suga. K. Muramatsu, T. Otaka, K. Atsumi amd R. Nishida. "9th Symposium on Photoelectronic Image Devices" Imperial College London September 1987.
- 5. EEV XQ1610 and XQ1615 series technical data sheets.
- 6. G.P. Hopkins 173rd Electrochemical Society meeting Las Vegas, Nevada October 1985.



FIG 1 TYPICAL SPECTRAL RESPONSE 400-2200 nm 25mm

WAVELENGTH mm





Orientation of PbO Crystallites













1000 – 2000 nm





TARGET VOLTS



FIG 8 TYPICAL LIGHT TRANSFER CHARACTERISTIC 25mm



TYPICAL AMPLITUDE RESPONSE





TYPICAL DELAY LAG CHARACTERISTICS

FIG 10

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Fig. 11. Thermal Image of Hot Soldering Iron.



Fig. 12. Hydrogen Flames at the end of a furnace Top: visible light Bottom: infra red





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Fig. 13. GaAs wafer at different stages of heat treatment taken with infra Red Leddicon in Bio-Rad IR1200 Polarising Infrared Macroscope. Photograph by courtesy of Dale Page, Bio-Rad Microscience Division.



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Fig. 14. A forged bank cheque detected by comparing (top), reflected visible light, with (bottom), infrared.

Nationwide Nationwide Anglia Building Society Anglia Princes Street Flex Account Swindon SNI 2HQ	08-60-86 <u>1 April 19 8 7</u>
Pay A.N. atter	ororder
the sum of Seventy Pounds Only	\$70-00
MR E W L TRAWNEY Chopee Number Son Code Accesses Number	n
* 10000 2* 08-6086* 0781834 ?*	



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