

## Photoconductive Imaging Using CuInSe<sub>2</sub> Film

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(Received June 7, 1993)

This paper describes an application for the first time of a vidicon type pickup tube using a chalcopyrite-type semiconductor copper-indium-diselenide (CuInSe<sub>2</sub>) film as a target for the image sensor. The fabricated sensor shows the horizontal resolution of 600 TV lines indicating that CuInSe<sub>2</sub> is one of promising materials for television image pickup device with the high resolution.

**KEYWORDS:** CuInSe<sub>2</sub> polycrystalline thin films, ionized cluster beam deposition, image pickup device, photoconductive imaging

### 1. Introduction

Chalcopyrite-type semiconductor copper-indium-diselenide (CuInSe<sub>2</sub>) has recently been attracting much attention because of a direct energy gap of around 1.0 eV and an absorption coefficient which is the highest reported to date for any semiconductors.<sup>1)</sup> Its proposed application is CuInSe<sub>2</sub>-based polycrystalline thin film solar cells, in which the conversion efficiency as high as 16.9% has been reported.<sup>2)</sup>

We report here, for the first time, an application of CuInSe<sub>2</sub> film to the photoconductive target of image pickup tube of vidicon type. We thought that CuInSe<sub>2</sub> could be applied to image pickup devices, as well as solar cells, since high efficient thin-film photoconductors are known to be useful in the photoconductive imaging.

The materials for this purpose are required to have a high resistivity in order to be used for storage type image sensing. The resistivity of CuInSe<sub>2</sub> films has been known to be strongly dependent on the In/Cu ratio.<sup>3)</sup> The smallest variation in the In/Cu ratio causes a large change in resistivity amounting to several orders of magnitude at the nearly stoichiometric composition. We reported that electrical resistivity of CuInSe<sub>2</sub> films could be controlled by changing various deposition parameters in three-source ionized cluster beam (ICB) technique.<sup>4)</sup> It is well known that In-rich films show much higher resistivity than Cu-rich films. We therefore used In-rich CuInSe<sub>2</sub> films prepared by ICB technique for an image pickup material.

### 2. Experimental

#### 2.1 Target Structure

A structure of the image pickup target is shown schematically in Fig. 1. The face plate is a 2/3-inch diameter circular glass plate coated with a dc-sputtered ITO electrode layer, on which a thin insulating film of approximately 20 nm in thickness was deposited to block an injection of holes. As the hole-blocking layer, we tested three kinds of materials, i.e., CeO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub> and SiO<sub>2</sub>, of which only the Si<sub>3</sub>N<sub>4</sub> was found to provide well-resolved images

as will be mentioned later.

High resistivity CuInSe<sub>2</sub> film of about 0.25 μm thickness was obtained by three-source ICB deposition. The source materials employed were Cu and Se of 99.999% purity and In of 99.9999% purity. The source temperatures of the three crucibles used to obtain In-rich CuInSe<sub>2</sub> of high resistivity were 1240°C for Cu, 270°C for Se, and 960°C for In. These CuInSe<sub>2</sub> films were deposited without the acceleration, since it is known that In-bombardment has no effect on improvement of the film quality.<sup>4)</sup> The substrate temperature was kept at  $T_s = 350^\circ\text{C}$  and the pressure in the vacuum chamber was maintained at  $0.4 \times 10^{-4}$  Torr. The thickness of the obtained film was approximately 0.25 μm for a deposition time of 10 min.

In conventional vidicon type image pickup tubes such as SATICON, an electron blocking layer of Sb<sub>2</sub>S<sub>3</sub> is used on the photoconductive layer. However, such layers often exhibit the photosensitivity themselves, which makes it difficult to know the effect inherent to CuInSe<sub>2</sub>. We therefore abbreviated this layer in the present experiment.

### 3. Results and Discussion

#### 3.1 Film Properties

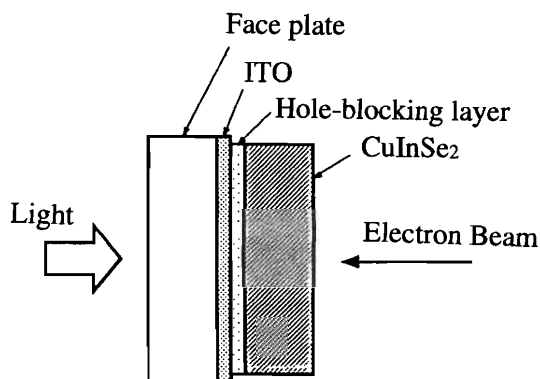


Fig. 1. Schematic illustration of the structure of CuInSe<sub>2</sub> vidicon target.

The X-ray diffraction pattern of obtained films are shown in Fig. 2. Peaks 112, 220 or 104 and 116 or 312, characteristic of the chalcopyrite phase, were observed. However, the film thickness ( $0.25 \mu\text{m}$ ) is so thin that the diffraction pattern suffers large background noises, making it difficult to detect extraneous binary phases.

The resistivity of this films was evaluated by the four-probe method. By this measurements, resistivity of  $2.4 \times 10^7 \Omega\text{cm}$  was obtained. However, this value is several orders of magnitude smaller than the value of  $10^{12} \Omega\text{cm}$  required for storage image sensing.<sup>5)</sup>

### 3.2 Image resolution

As mentioned before, three different types of thin layers such as  $\text{CeO}_2$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{SiO}_2$  were tested as hole-blocking layers. Among these films, only  $\text{Si}_3\text{N}_4$  provided a well-resolved image, suggesting that only the  $\text{Si}_3\text{N}_4$  film acts as a hole blocking layer.

### 3.3 Dependence of signal and dark currents on the target voltage

The signal and dark current rapidly increased and eventually saturates with increasing target voltage. However the dark current is 10 times as large as signal current. This implies that electron injection is not blocked. This characteristics would be improved by the use of an appropriate electron blocking layer.

### 3.4 Spectral response

The spectral photoresponse measured with the constant photon-energy spectrometer is illustrated in Fig. 3, showing a considerable flatness between infrared to green wavelength region, followed by gradual decrease in blue region. We compare the photoresponse with other materials: The peak of the photoresponse curve in amorphous Si:H lies between 520 and 580 nm,<sup>6)</sup> the peak in amorphous Se lies between 380 and 480 nm<sup>7)</sup> and that of GaAs lies between 800 and 900 nm.<sup>8)</sup> Contrary to these materials,  $\text{CuInSe}_2$  shows a considerably flat response covering from infrared to near ultraviolet region. This result has a good agreement with the photoconductivity spectrum reported in In-rich  $\text{CuInSe}_2$  films.<sup>4)</sup>

### 3.5 Resolution

Figure 4 shows a resolution pattern taken by the image pickup tube using the above-mentioned film for the

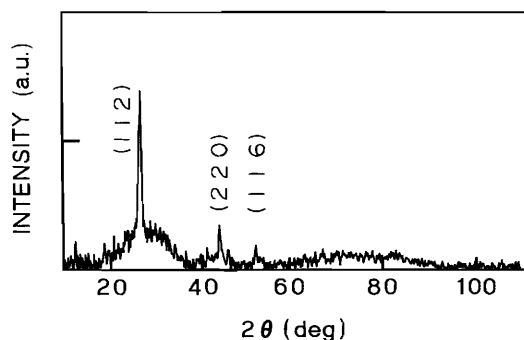


Fig. 2. The X-ray diffraction patterns obtained in In-rich  $\text{CuInSe}_2$  film.

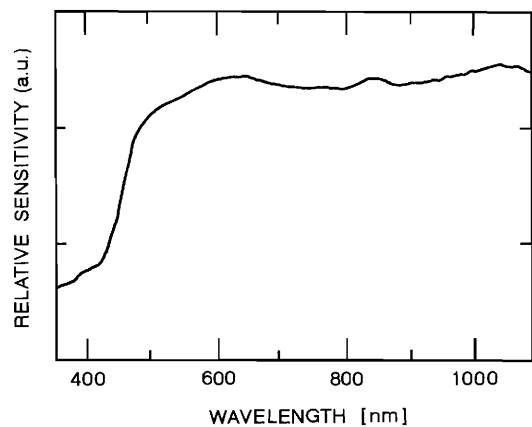


Fig. 3. Spectral photoresponse of In-rich  $\text{CuInSe}_2$  vidicon target with target voltage  $V_t = 65 \text{ V}$ .

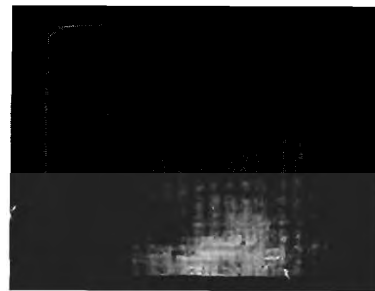


Fig. 4. Video image taken by In-rich  $\text{CuInSe}_2$  vidicon. Horizontal resolution of more than 600 TV lines is observed.

target. The horizontal resolution of 600 TV lines is observed. However, the amplitude response of this target could not be obtained due to poor signal current compared with the dark current. The horizontal resolution obtained is sufficient for conventional use, although the resistivity of the film is much smaller than that required for the photoconductive imaging. This can be explained if one takes into account the film thickness of only  $0.25 \mu\text{m}$ , which makes the target resistance higher.

### 3.6 Time response

The target showed a good time response with a short lag. The accurate value of the lag could not be measured since it was less than the time-resolution of the measuring system.

The short lag may be attributed either to the reduction of the beam-discharge lag by the large dark current or to the photoconductive lag due to the filling of traps by the dark current.

## 4. Conclusion

We have for the first time obtained the photoconductive imaging using thin films of  $\text{CuInSe}_2$ . The spectral photosensitivity of the device covers the whole visible region. The horizontal resolution of 600 TV lines is observed. Therefore, it is elucidated that  $\text{CuInSe}_2$  is one of promising materials for TV image pickup device because of the flat spectral response and the high resolution. We believe we can improve the dark current problems by in-

creasing the resistivity of the film and by an appropriate use of an electron-blocking layer. These will be objectives of future investigation.

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