Preparation and characteristics of CuGaSe2/CdS solar cells

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# ADVERTISEMENT



Because the CFT sensor cannot be fully encapsulated, it will be more susceptible to long-term contamination than encapsulated MOS devices. Deposition of suitable passivation layers over the gate oxide and/or over the entire chip may be required. Of course, the thin film of resistive material may itself be useful for passivation. Our first PFI-coated devices have not exhibited threshold voltage drift on a time scale of months with the devices operated in normal ambients at room temperature.

Even with passivation, the application of the sensing film is the final processing step. Our particular polymer films are spun on from solution but the CFT could also be made with evaporated, sputtered, or even sprayed-on films. Thus MOS-compatible and MOS-integrable sensing devices can now be made from materials which previously could only be used in discretedevice form.

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- details.

# Preparation and characteristics of CuGaSe<sub>2</sub>/CdS solar cells

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p-CuGaSe<sub>2</sub>/n-CdS heterojunctions have been prepared by depositing CdS films on p-type CuGaSe<sub>2</sub> single crystals whose initial resistivity was  $10^{-2} \Omega$  cm and changed to 1  $\Omega$  cm after the CdS film deposition. The CdS films, which were grown by a multisources method, exhibit a room-temperature resistivity of 0.1  $\Omega$  cm. The absolute quantum efficiency of these devices as photovoltaic detectors reaches the value of 80% at a wavelength of 5800 Å. As solar cells, these heterojunctions at 25°C display a solar power conversion efficiency of 5% when they are exposed to the solar light whose intensity is 71 mW/cm<sup>2</sup>. When the heterojunctions are directly polarized, they emit light in a broad band which is centered at ~7700 Å. An external electroluminescent emission efficiency of about 0.05% has been measured at liquid-nitrogen temperature.

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The I-III-VI compounds are particularly suitable for making p-n heterojunctions with the II-VI compounds. In fact, they present a structure which is similar to that of the II-VI compounds. They can also have p-type conductivity, while the II-VI compounds can generally have only n-type conductivity. Up to now, only two types of heterojunctions between the I-III-VI and the II-VI compounds have been prepared. The former, which is the heterojunction p-CuInSe<sub>2</sub>/n-CdS,<sup>1</sup> exhibits, as a photovoltaic detector, a uniform quantum efficiency of 70% between 0.55 and 1.25  $\mu$ , while, as a solar cell, can have a solar power conversion efficiency of 12%.<sup>2</sup> The latter, which is the heterojunction p-CuGaS<sub>2</sub>/n-CdS, emits green light with an external quantum efficiency of ~0.1% at  $77^{\circ}$ K<sup>3</sup> when directly polarized.

Here, we refer to another heterojunction between I-III-VI and II-VI compounds which was prepared by depositing low-resistivity CdS films on  $CuGaSe_2$  substrates by a method which is different from that used to prepare the above-mentioned heterojunctions.

The  $CuGaSe_2$  crystals, which we used as substrates, have been grown by the method of vapor-phase transport and iodine was used as a transport agent. The asgrown crystals present a face which is perfectly smooth, while the other face is rough. The rough face was

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FIG. 1. I-V characteristic of a p-CuGaSe<sub>2</sub>/n-CdS heterojunction in the dark and at room temperature.

lapped, and subsequently two evaporated gold contacts were made on it to control the substrate resistivity before and after the deposition of the film. In fact, it has been observed that the resistivity of the substrates, which was  $10^{-2} \Omega$  cm before the film deposition, increased about two orders of magnitude after the film deposition. This resistivity increase could be due to a temperature-controlled relaxation of acceptors, as was supposed by Wagner for CuGaS<sub>2</sub>.<sup>4</sup> Hall-effect measurements have been made on some CuGaSe<sub>2</sub> crystals. They were *p* type with Hall mobility of 15 cm<sup>2</sup> V<sup>-1</sup> sec<sup>-1</sup>.

The CdS films were deposited, by employing a suitable mask, on to the as-grown smooth face of the CuGaSe<sub>2</sub> crystals. Before CdS deposition the substrates were etched in a 1:10 solution of HF and deionized water and subsequently rinsed in deionized water. The CdS films were prepared in a vacuum of  $\sim 10^{-6}$  Torr by evaporating Cd and S from two different sources and by controlling the evaporation rate of the two elements with a quartz crystal thickness monitor. During the deposition the substrate was kept at 200°C. After observing that the lowest resistivity obtainable in such films was of about  $10^2 \Omega cm$ , we evaporated In from a third source during the film deposition in order to dope the film. By using a ratio between the evaporation rates of Cd and S of  $\sim 1.2$  and an In doping of about 2%, films whose resistivity was  $0.1 \Omega$  cm or less, were obtained with very good reproducibility. A film thickness of about 10  $\mu$  was obtained after 1 h deposition. The CdS films were polycrystalline with a grain dimension of 0.5  $\mu$ . Hall-effect measurements, which were made on CdS films deposited on mica, gave a Hall mobility of 0.3  $\text{cm}^2 V^{-1} \text{sec}^{-1}$ . The contacts on the CdS films were made by evaporating In under high vacuum.

The I-V characteristic of a p-CuGaSe<sub>2</sub>/n-CdS heterojunction, whose area was 2.5 mm<sup>2</sup>, obtained in the dark and at room temperature, is displayed in Fig. 1. A



FIG. 2. Absolute quantum efficiency as a function of the wavelength for a p-CuGaSe<sub>2</sub>/n-CdS heterojunction photovoltaic detector. The curve has been obtained without any bias applied.

rectification factor of  $10^4$  is obtained when 2 V are applied. The current with direct polarization follows a relation of the type  $I \propto \exp(eV/nkT)$ , where *n* is about 1.86. The behavior of the absolute quantum efficiency at zero bias as a function of the wavelength which was used to illuminate the heterojunction is reported in Fig. 2. The absolute quantum efficiency was measured by employing the line of 6764 Å of a krypton laser, while the photocurrent spectrum was obtained by a tungsten lamp and a monochromator and then normalized with the absolute quantum efficiency measured by the 6764-Å line of the krypton laser. As one can see, a quantum efficiency of 80% is obtained at 5800 Å. By exposing this heterojunction to the solar light, whose intensity measured by a calibrated Si solar cell was 71



FIG. 3. Photocurrent-photovoltage characteristic of a p-CuGaSe<sub>2</sub>/n-CdS solar cell when it was exposed to the solar light whose intensity was 71 mW/cm<sup>2</sup>.

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mW/cm<sup>2</sup>, a solar power conversion efficiency of 5% has been obtained without any antireflecting coating at 25 °C. The calibrated Si solar cell, which exhibits a solar power conversion efficiency of 10%, was supplied from Solarex, Rockville, Md. The exposed area of the CuGaSe<sub>2</sub>/CdS solar cell was carefully measured by an optical microscope. The curve, which represents the photocurrent as a function of the photovoltage, when the heterojunction is exposed to 71 mW/cm<sup>2</sup> solar light, is displayed in Fig. 3. The fill factor of this solar cell is 0.55.

The heterojunction  $CuGaSe_2/CdS$  is electroluminescent when it is directly polarized and emits light in a broad band which is centered at 7700 Å with an external efficiency of 0.05% at liquid-nitrogen temperature. This emission is probably due to the injection of electrons from CdS into  $CuGaSe_2$  where they recombine with the holes which are trapped in a level localized in the forbidden gap near the valence band.

The limited solar power conversion efficiency which was obtained with the heterojunction  $CuGaSe_2/CdS$  is probably due to the high lattice mismatch between  $CuGaSe_2$  and CdS (3.8%).

Lattice mismatch of this order can introduce a high density of energy states within the band gaps of the two materials. In this case, the dark current of the device can be due mainly to tunneling via interface states. A tunneling mechanism for the CuGaSe<sub>2</sub>/CdS heterojunction was confirmed by measurements of dark J-V characteristics as a function of the temperature. In fact, in the range 77-300°K the slope of  $\ln J$  versus V remained unchanged. When the current is dominated by tunneling or tunneling-recombination mechanisms, the reverse saturation current is high and this can limit both the open-circuit photovoltage and fill factor in solar cells.

A better selection of materials between the I-III-VI and II-VI compounds, such as  $CuInS_2$ , which has a forbidden gap of 1.5 eV close to the optimum for the solar power conversion<sup>5</sup> and ZnSe which has a larger gap than CdS, can give the possibility of realizing solar cells with higher efficiency. The lattice mismatch between CuInS<sub>2</sub> and ZnSe is limited to 2%.

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# GaAs lasers with consistently low degradation rates at room temperature

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Simple oxide-insulated stripe-geometry double-heterostructure lasers have been made and life tested as part of an extensive laser reliability program. Early lasers have now been on test for more than 13000 h and the first batch test has exceeded 7000 h. All the batch test lasers show slow degradation and at least 85% have rates of increase of threshold below 3.3% per 1000 h. Simple visual prebonding selection was used to eliminate defective lasers, and these results demonstrate that within this limitation lives in excess of 7000 h can be consistently achieved.

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With the aim of developing reliable lasers for fiberoptic communications simple oxide-insulated stripegeometry double-heterostructure lasers have been made and an extensive program of life testing has been initiated. Early lasers have now exceeded operating lives of 13 000 h, and the first batch of 20 lasers has been on test for more than 7000 h. All the lasers on the batch life test show slow degradation and at least 85% are degrading so slowly that they will clearly continue to operate well beyond 10 000 h. Selection before chip bonding was used to eliminate bad material. These results demonstrate that within this limitation lives in excess of 7000 h can be achieved consistently. Several reports<sup>1-3</sup> of lives of this order have been published and recently<sup>4</sup> operation has been obtained for 8500 h at the elevated temperature of 70 °C but problems exist with reproducibility if every laser produced is life tested. The significance of the present work is its demonstration that by prebonding selection long life can be expected on a very high proportion of lasers.

The emphasis of this work has been on maintaining a high standard of laser fabrication technology and perfection of wafer growth. The laser selected was a simple oxide-insulated stripe geometry using a doubleheterojunction layer structure. Early lasers showed a

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