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Citation: *Applied Physics Letters* **46**, 266 (1985); doi: 10.1063/1.95652

View online: <http://dx.doi.org/10.1063/1.95652>

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Laser-induced synthesis of thin CuInSe_2 films

M. C. Joliet, C. Antoniadis, R. Andrew, and L. D. Laude

Faculté des Sciences, Université de l'Etat, Mons, Belgium

(Received 25 September 1984; accepted for publication 5 November 1984)

Thin films of CuInSe_2 are synthesized by laser irradiation of Cu-In-Se sandwiches in 1:1:2 atomic proportion. Using transmission electron microscopy (TEM), electron diffraction, and optical spectrometry, the presence of semiconducting ternary compound CuInSe_2 , with the chalcopyrite structure, is strongly evidenced in all the irradiated samples, supported or not, with no other phases observed. For glass-supported films, the optical absorbance characteristic of a uniformly transformed region indicates a direct optical band gap of (0.95 ± 0.10) eV. Crystallites obtained on free-standing films (i.e., supported on TEM grids) can reach $20 \mu\text{m}$ in dimension.

The technique of laser irradiation of multilayer elemental films for the production of binary semiconductor thin films has previously been applied with success to the systems AlSb , AlAs , CdTe , CdSe ,¹⁻³ GeSe , and GeSe_2 .⁴ In this work we choose to examine, by the same technique, the formation of the ternary compound CuInSe_2 . Belonging to the I-III-VI₂ group, CuInSe_2 has already proven its suitability for photovoltaic applications due to its excellent optical and transport properties.^{5,6} The situation here is more complex than those cited above because of the competition between the formation of laser synthesized CuInSe_2 and the several possible binary compounds like Cu_2Se , CuSe , In_2Se_3 , InSe , In_2Se .⁷ Moreover, the melting points T_m of the elemental constituents are very different (copper, $T_m = 1356$ K; indium, $T_m = 429$ K; selenium, $T_m = 490$ K). So, in order to test the feasibility of the laser-induced synthesis of this ternary compound, two regimes are considered: (i) nonsupported films irradiated under "pulsed" conditions ($t = 0.7$ s); (ii) scan-irradiated films deposited onto glass substrates. The results are analyzed by optical spectrometry for supported films only and by transmission electron microscope (TEM) and electron diffraction for both regimes.

1000-Å-thick films composed with single layers of copper, indium, and selenium in a 1:1:2 atomic proportion are successively vacuum evaporated onto either glass substrates or freshly cleaved NaCl crystals using a multicrucible electron gun source in a vacuum of $\sim 10^{-6}$ Torr. Elemental layer thicknesses are controlled by a quartz monitor to a precision of 1%-2%. The films are protected against air between two SiO_2 layers ~ 150 Å thick. Films condensed onto salt are floated off and transferred onto TEM copper grids with an $80 \mu\text{m} \times 80 \mu\text{m}$ mesh size and are in the following called free-standing films. All films are irradiated in air using an Ar^+ laser operating on all green lines (457.9–514.5 nm). The spatial profile of the beam is Gaussian, with a diameter ($1/e^2$) on the sample of 1.6 mm. Free-standing films are irradiated for 0.7 s by chopping the laser beam mechanically. They are treated with varying power density through a diaphragm in order to irradiate reasonably homogeneously a 1-mm-diam spot. A raster scan with an horizontal scanning speed of 2 mm/s and a vertical one of $40 \mu\text{m/s}$ allow the irradiation, at various power densities, of the glass-supported films, thereby producing areas, several square cm in extent, the homogeneity of which is ensured by inserting a cylindrical lens in the beam. Portions of these samples are detached by a collo-

dion pull, and mounted on TEM grids for subsequent analysis.

Irradiation of a free-standing film at a power of ~ 3 W (slightly above the threshold of transformation) results in the formation of a polycrystalline film as depicted in Fig. 1(a). Grain size varies between 0.1 and $1 \mu\text{m}$ for this kind of sample but depends strongly on the power density. The corresponding high resolution electron diffraction (HRED) pattern from an $80 \mu\text{m} \times 80 \mu\text{m}$ grid hole is superposed on Fig. 1(a). The associated microdensitometer trace shows that the film is only composed of the chalcopyrite (tetragonal) structure of CuInSe_2 (Ref. 8) with no evidence of any remaining elemental constituents, nor any of the various possible bina-

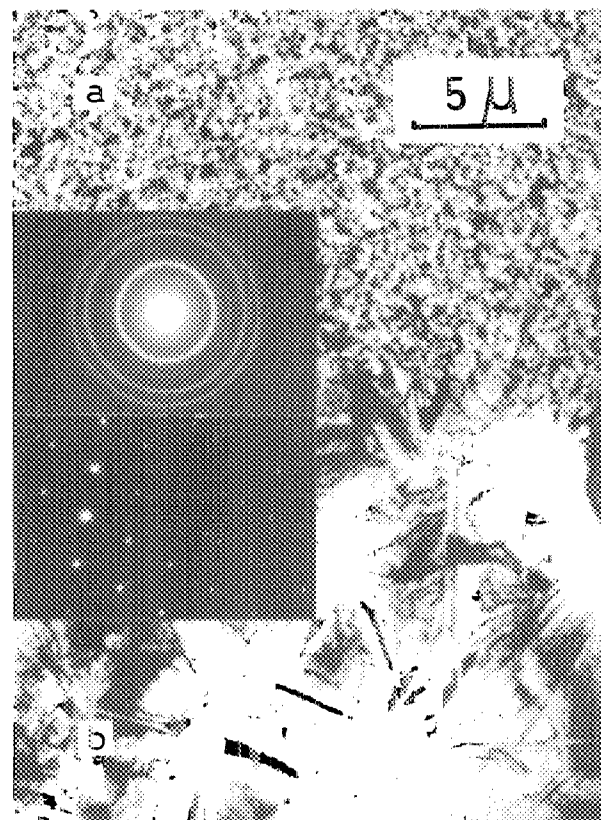


FIG. 1. Bright-field TEM micrographs of 1000-Å-thick multilayered Cu/In/Se film after laser irradiation: (a) polycrystalline structure obtained with a power slightly above threshold of formation ($P = 3$ W) and corresponding HRED pattern (on a $80 \mu\text{m} \times 80 \mu\text{m}$ grid hole); (b) single crystal platelets obtained with a higher power ($P = 5$ W) and their electron diffraction pattern (beam of a few μm diameter).

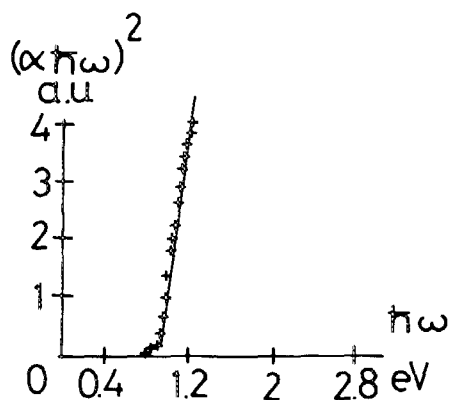


FIG. 2. Optical absorbance of scan-irradiated CuInSe_2 film.

ry compounds in this system. At a beam power exceeding ~ 5 W the central part of each grid hole is composed of much larger, heavily twinned, crystals as appearing in Fig. 1(b). Crystal dimensions here can reach $20\ \mu\text{m}$ and electron diffraction from such zone also clearly identifies CuInSe_2 . The pattern associated with Fig. 1(b) shows in particular tetragonal CuInSe_2 with the $[201]$ zone axis parallel to the electron beam. Extra spots on this picture are due to twin reflections. Other orientations, as for example the $[241]$ and $[1\bar{1}\bar{1}]$ zone axes, have also been observed and, in general, there does not appear to be preferential orientation as in the case of GeSe_2 .⁴ The central part of each grid hole is in every case surrounded by polycrystallites appearing since a part of the energy given by the laser is probably absorbed through the copper grid bars. In general we can say that the grain size of laser synthesized CuInSe_2 on free-standing films depends strongly on the laser power, dimension varying from $100\ \text{\AA}$, at the threshold of transformation, which has been determined to be equal to (1.2 ± 0.1) W, up to $20\ \mu\text{m}$ at $P \sim 5$ W. Variations in the layer sequence do not detectably influence the film resulting from irradiation although the threshold irradiation power may vary with film reflectivity. Detached fragments of glass-supported scan-irradiated films are polycrystalline with grain sizes ~ 0.1 – $1\ \mu\text{m}$, this size being at first sight independent of beam power. Diffraction data, however, present also reflections due only to tetragonal CuInSe_2 . Preliminary experiments on nonstoichiometric proportions tested up to $\sim 10\%$ – 20% deviation have also been done with the result that the ternary compound is also formed here. Additional rings present in the HRED pattern from those films could not be identified as due to any of the reported binary compounds in the system. Areas of scan-irradiated films are examined by optical spectrometry from 600 to 2200 nm. Figure 2 shows the plot of $(\alpha\hbar\omega)^2$ vs $\hbar\omega$, indicating a direct gap at around 0.95 ± 0.10 eV in agreement with published data for CuInSe_2 .^{9–11}

Quite clearly the irradiated films are composed of the ternary compound CuInSe_2 . Since the phase diagram⁷ of this

system is not particularly simple, it may appear surprising that the compound forms so easily without traces of the alternative binary compounds. As with the binary systems previously studied,^{1–4} the final result is controlled by the overall stoichiometry of the film and any slight excess due to the inherent inaccuracy of the deposition method is presumably swept to the grain boundaries where they are so widely dispersed that they show no trace in electron diffraction. The temperature achieved during the irradiation is not easily calculated since reflectivity, transmission, and thermal conductivity during irradiation are time dependent in an unknown way. Moreover, individual film thicknesses are of the order of 200 – $300\ \text{\AA}$ and, it is known that the actual melting temperature of such films is lower than the bulk melting temperature.¹² Irradiation of free-standing films above ~ 5 W produces particularly large CuInSe_2 crystals, with a rather sharp boundary between these and the surrounding polycrystalline zone. The situation is not dissimilar to the creation of explosively crystallized regions in a poly-matrix when amorphous Ge films are irradiated above a certain threshold. The heat of formation of CuInSe_2 can therefore be expected to play a similar role to the heat of crystallization in the case of Ge or binary compounds.^{2,3} Substrate supported films exhibit, in these preliminary experiments, a disappointingly small crystal size. However, the direct fundamental absorption edge at 0.95 eV is in good agreement with the gap reported for CuInSe_2 .^{9–11}

So in conclusion, these promising results, allied to the current interest in CuInSe_2 as a photovoltaic material, suggest further work along these lines which are already in development.

The authors would like to thank M. Wautelet for very helpful discussions. This work is partially supported by program of "Institut de recherche sur les Interfaces Solides" and by the National Energy Program of the Belgian Ministry for Science Policy, Brussels.

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