Adjacent compensated codoping (alloying) of semiconductor films and its application to CdTe and CdS

Sergio J. Jiménez-Sandoval[1*], Abraham I. Calderón-Martínez[1], Omar Jiménez-Sandoval[1], Miguel Gómez-Álvarez[1], Francisco Rodríguez-Melgarejo[1], Martín A. Hernández-Landaverde[1], Francisco J. Flores-Ruiz[2]

[1] Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Unidad Querétaro, Libramiento Norponiente No. 2000, Real de Juriquilla, Querétaro, Qro. 76230, Mexico

[2] CONACYT-Instituto de Física, Benemérita Universidad Autónoma de Puebla, Av. San Claudio, s/n, Puebla, Pue., Mexico

*Author to whom correspondence should be addressed: sergio.jimenez@cinvestav.mx

Supplementary Information

Table S1. Thickness of the CdTe:(Ag+I) films for the indicated concentrations of AgI in the target.

AgI concentration in the target (at.%)	0	0.5	1.0	3.0	4.0	5.0	6.0	7.0
Thickness (μm)	1.13	1.10	0.98	1.3	1.7	1.47	0.87	0.85

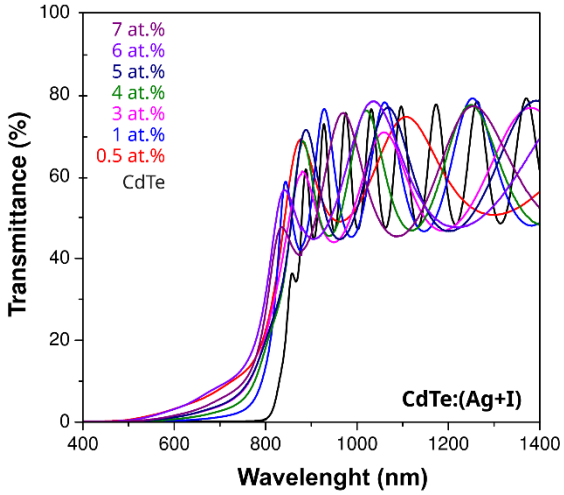

Fig. S1. Optical transmittance of the CdTe:(Ag+I) films in the range from 200 to 1400 nm. The apparent displacement of the absorption edge is due to the lower thickness of the films. In Fig. 5b in the main text, the spectra are shown with a vertical displacement for clarity purposes.

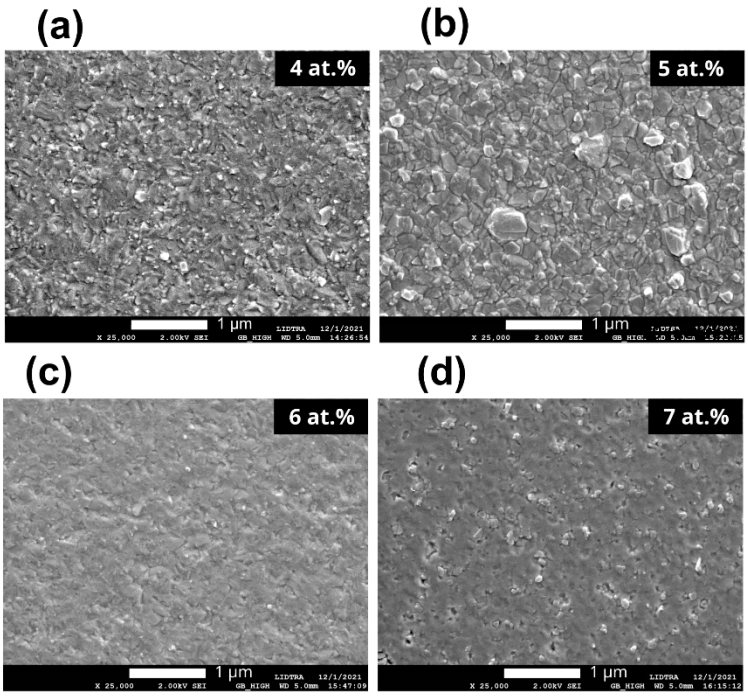

Fig. S2. Scanning electron microscopy (SEM) images of the surface of the CdTe:(Ag+I) films with adjacent codopants concentration of (a) 4 at.%, (b) 5 at.%, (c) 6 at.% and (d) 7 at.%. The white bar corresponds to one micrometer.

Table S2. Values of the cubic lattice parameter a, strain ($S=\Delta a/a_0$) and thickness of the CdTe:(In+Sb) films for the indicated concentrations of InSb in the target. The strain was calculated with respect to the lattice parameter of the CdTe film (not with respect to the value of the single crystal).

InSb concentration in the target (at.%)	4	5	6	7
Lattice parameter *a* (Å), cubic phase	6.4897	6.4943	6.4961	6.4995
S (%)	0.0014	0.0007	0.0004	0.00007
Thickness (µm)	1.45	1.38	1.40	1.20

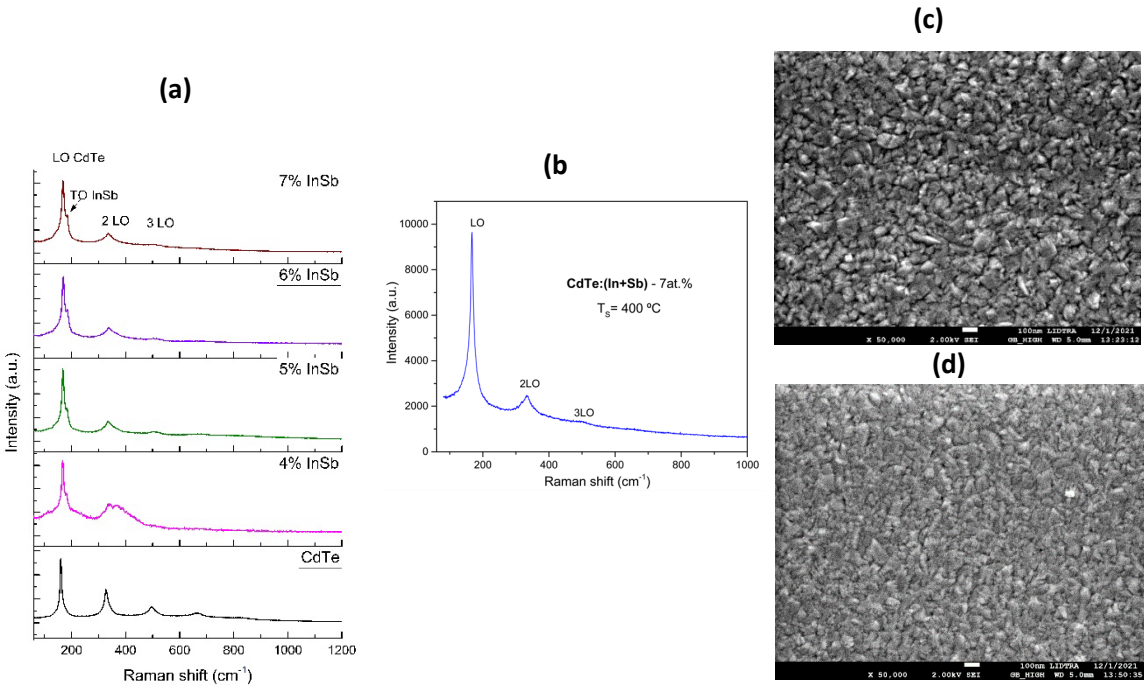

Fig. S3. (a) Raman spectra of the films grown at 275 ºC for the indicated concentrations of InSb in the sputtering target. (b) Raman spectrum of CdTe:(In+Sb)-7 at.% grown at 400 ºC. SEM image of CdTe:(In+Sb) films with (c) 5 at.% InSb and (d) 6 at.% InSb. The white bar corresponds to 100 nm.

Terahertz spectroscopy

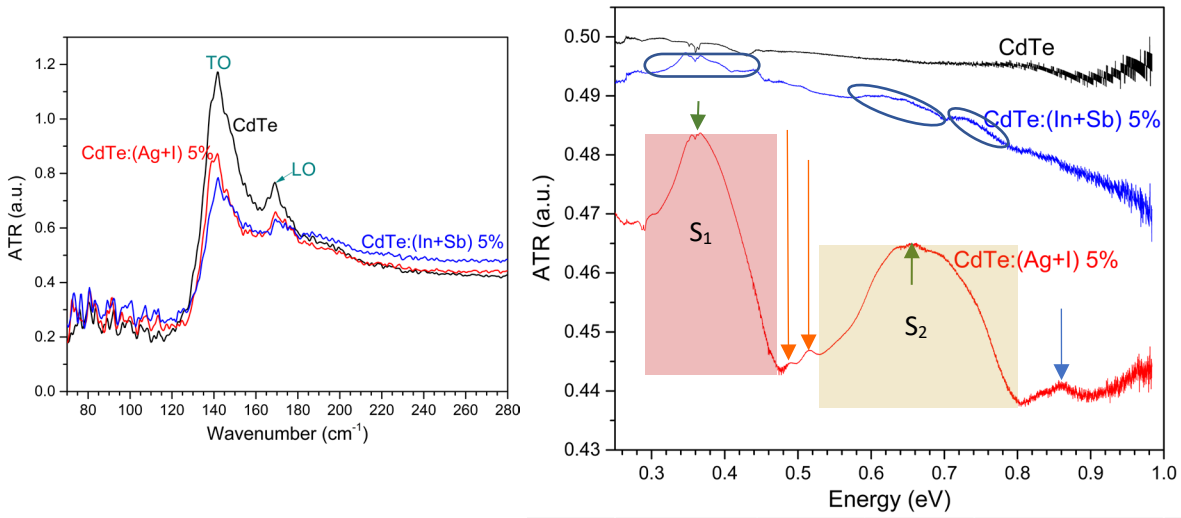

Fig. S4. Attenuated total reflection (ATR) terahertz spectroscopy absorbance measurements of CdTe, CdTe:(Ag+I)-5 at.% and CdTe:(In+Sb)-5 at.% films. (a) The transverse optical (TO) and longitudinal optical (LO) phonons of the CdTe host are observed at 142 and 169 cm^{-1}, respectively. (b) Spectra from 0.25 eV (2000 cm^{-1}) to 0.98 eV (7900 cm^{-1}). The spectrum of CdTe did not present any absorption features in this energy range. In the spectrum of CdTe:(In+Sb)-5% weak bands, indicated by the blue elongated shapes, were observed. The small sharp features in the spectra denoted with asterisks are remnants of the subtraction of the substrate spectrum. Two well-defined bands centered at 0.36 eV (S_1) and 0.66 eV (S_2) appeared in the spectrum of CdTe:(Ag+I)-5%. The widths of these bands were different (highlighted).

The ATR absorbance spectrum of CdTe:(Ag+I)-5 at.%, Figure S4b, presented two well-defined bands, S_1 and S_2, centered at 0.36 eV and 0.66 eV, respectively. Three low-intensity features L_1 (0.49 eV), L_2 (0.52 eV) and L_3 (0.86 eV) were also observable. Two energy diagrams describing the absorption features S_i and L_i are proposed below. The diagrams were generated taking into account the following considerations:

1. When the photon energy equals the difference between a level occupied by an electron and that of an empty higher energy level, the electron can be excited to the upper level so that an absorption process is registered. However, the detection of absorption events does not provide unambiguously the position of the participating levels with respect to the edges of the valence and conduction bands. Only the energy difference between the initial and final states is determined. Reasonable assumptions have to be made in order to elaborate a coherent energy diagram describing the experimental absorbance spectrum.
2. Given the way that adjacent codopants were selected, it can be assumed that the sub-band closer to the conduction band (CB) was formed by iodine atoms (n-type impurities), and that the sub-band closer to the valence band (VB) was created by the silver atoms (p-type impurities).
3. The optical transitions are direct (CdTe is a direct band gap semiconductor).

4. The value of the electron affinity of CdTe is χ= 4.3 eV. The work function measured for the film with 5 at.% AgI was 4.7 eV (this work, Figure 8e in the main text). From these values, the Fermi energy lies 0.4 eV below the CB edge. Additionally, the work function of the pristine CdTe films was 5.6 eV (this work, Figure 8e), in accordance with reported data for this material.

5. The width of the sub-band S_2 is larger than the width of the sub-band S_1. Although this difference may be caused by several factors (for example, the inter-level separation, does not have to be identical in each sub-band), it is pointed out that the concentration of Ag in the CdTe:(Ag+I)-5 at.% films was slightly larger than that of I, as indicated by the chemical composition, Figure 6d. That is, the larger number of silver atoms could generate a larger number of impurity levels than those produced by the iodine atoms. Should this be the case, the broader sub-band would be the acceptor one, provided the inter-level separations in each sub-band were similar.

From these considerations, the energy diagrams in Figure S5 are proposed for describing the absorption processes in the spectrum of the film codoped with (Ag+I)-5 at.% in Figure S4b. The diagrams were made to scale, considering the energy of the transitions, the measured band gap and work function of CdTe:(Ag+I)-5 at.%, and the measured work function of CdTe. The reported electron affinity of CdTe is 4.3 eV. In Figure S5a the absorbance bands depicted at the right-hand side present the same order as they appear in the spectrum in Figure S4b. Figure S5b presents an alternative energy diagram for the observed absorbance data. Both diagrams are compatible with points 1-4 above, while only the diagram S5b is in accordance with point 5.

The following observations, derived from the electrical and photoconductivity results, favor the band diagram in Figure S5b as more appropriate for describing the ATR spectrum of the CdTe:(Ag+I)-5% film in Figure S4:

i) The Fermi energy of the sample is 0.4 eV below the CB edge. When the film and the CuTe contact is applied, the contact work function and the film Fermi energy level-up, as depicted by the brown symbols on the left in Figs. S5a and S5b.

ii) Thus, the relative position of the Fermi level (highest occupied level) in S5a and S5b, with respect to the CB and the upper (iodine) band, implies that the transport of photo excited electrons can occur in S5a only through the CB. In the diagram S5b, on the other hand, the charge transport can occur not only through the empty states in the S_1 (iodine) sub-band, but also through the CB. In diagrams S5a and S5b the barrier height (ϕ_b) between the contact and the CB is $\approx$ 0.55 eV. In S5b the barrier height between the contact and the empty states in S_1 above E_F is significantly lower: $\approx$ 0.15 eV.

iii) Experimentally the contact between CuTe and CdTe:(Ag+I)-5 at.% is ohmic Figure 8c. This result is consistent with diagram S5b, in which electrons pass through a small barrier and move through the states in sub-band S_1. In order for electrons to reach the CB, they must gain enough energy to overcome the barrier ($\approx$ 0.55 eV). This energy can be provided if the film receives photons with larger than 0.55 eV, as in the photoconductivity experiments.

From this analysis, the discussion of the terahertz spectroscopy data in the main text considers the energy diagram in Figure S5b. In addition, the (donor) sub-band S_1 is identified as S_d, and the (acceptor) sub-band S_2 as S_a.

Additional information on the energy distribution of the energy levels inside the band gap was provided by the (80 K) photoluminescence experiments. Figure 6c shows the deconvolution of the PL spectrum for the CdTe:(Ag+I)-5 at.% film, where three emissions below the band edge were evident. These levels are indicated tentatively in diagrams S5a and S5b below the CB edge. In diagram S5b the position of the Fermi level near the bottom of the donor sub-band implies that most of the levels in this sub-band are empty. The empty levels were created when electrons from the donor atoms (iodine) made transitions to the available lower energy levels in the acceptor (silver) sub-band. That is, the acceptor sub-band would be occupied by electrons originating from the donor atoms. In both diagrams in Figure S5, the probability that electrons from the VB make transitions to the acceptor sub-band is negligible since the energy required is too large for thermal excitations or quantum tunneling. An empty, or nearly empty, donor sub-band was possible because a) compensating impurities were employed (forming two sub-bands in the band gap), and b) the acceptor sub-band was deep so that it cannot be occupied by electrons from the valence band.

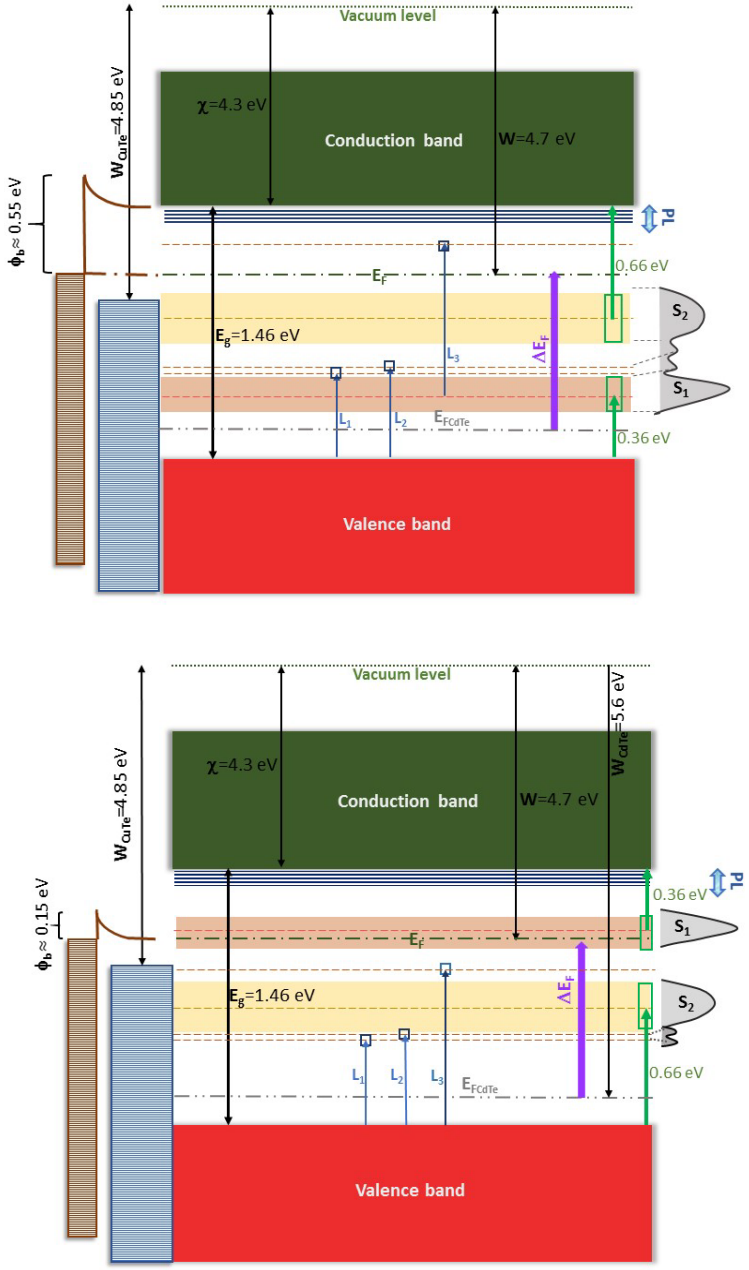

Fig. S5. Proposed band diagrams consistent with the absorbance spectrum of the CdTe:(Ag+I)-5 at.% film in Figure S4b. Both diagrams were elaborated to scale considering the values of the band gap energy of the CdTe host (1.46 eV for this particular sample) and of the absorbance sub-bands. The reported electron affinity for CdTe is 4.3 eV; the work function of the film (4.7 eV) was measured by Kelvin probe force microscopy (this work, Figure 8e, main text). The ATR features in Figure S4b are depicted at the right-hand side of each diagram. The transitions L_i in (b) are tentative and consider that the excited electrons depart from the valence band. The electrical contact with CuTe, used for the Hall effect and photoconductivity measurements, is represented on the left-hand side of each diagram with brown symbols. The energy levels close to the CB edge correspond to emissions detected by photoluminescence experiments, Figure 6c, and to the activation energies obtained from temperature dependent Hall effect measurements, Figure S6.

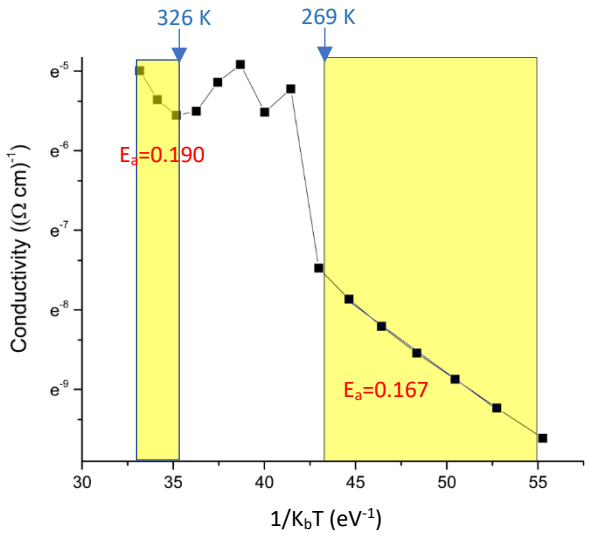

Fig. S6. Arrhenius plot for the conductivity of the CdTe:(Ag+I)-5 at.% film. Two activation energies with values of 0.190 and 0.167 eV were defined. In the temperature range between 269 and 326 K the conduction mechanisms cannot be described by a single energy barrier with an activation energy.

Table S3. Thicknesses of the CdS:(Ag+Cl) films for the different concentrations of AgCl in the sputtering target.

AgCl concentration in the target (at.%)	0	0.5	1.0	2.0	3.0	4.0	5.0
Thickness (nm)	110±5	90±4	95±7	87±2	76±8	86±10	80±4

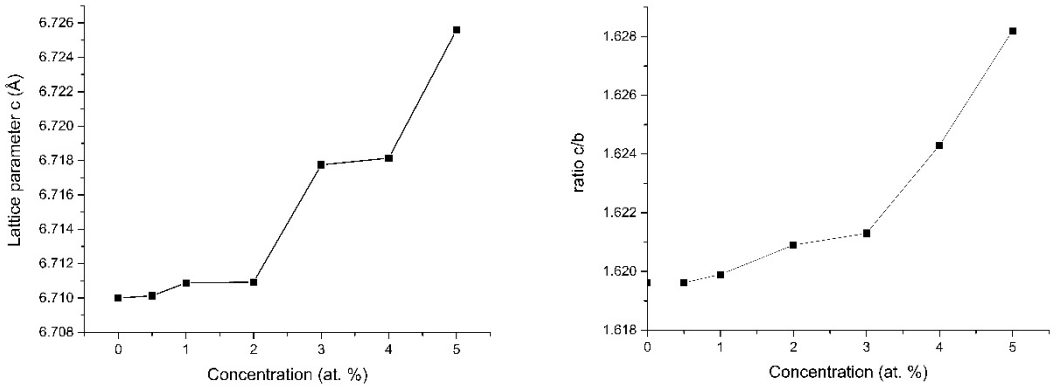

Fig. S7. (a) Lattice parameter *c*, and (b) ratio *c/b* of the CdS films as a function of the concentration of AgCl in the target.

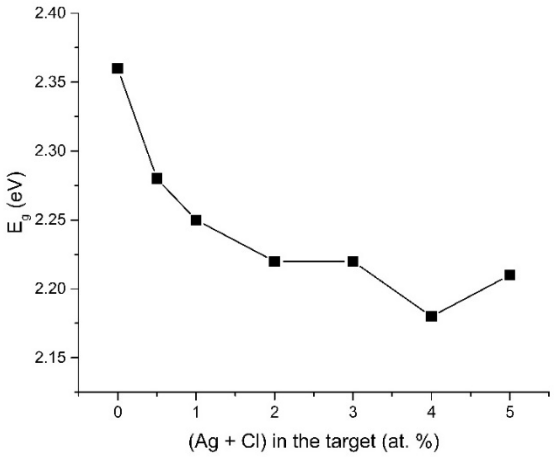

Fig. S8. Room temperature band gap of the CdS:(Ag+Cl) films obtained from Tauc´s plots as a function of the AgCl concentration in the sputtering target.

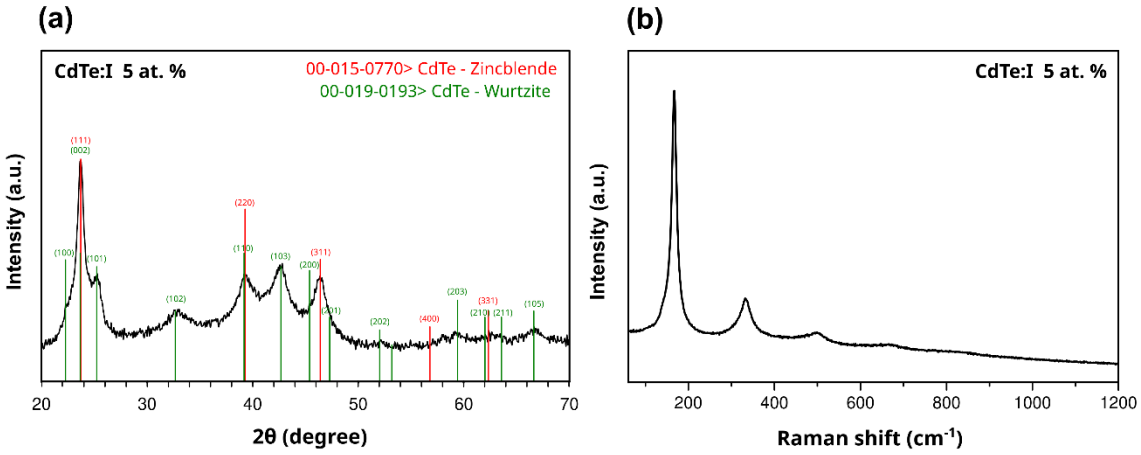

Figure S9: (a) X-ray diffraction pattern and (b) Raman spectrum of a CdTe:I film deposited at 275º C from a sputtering target made of a mixture of CdTe and CdI_2 powders; the latter at a concentration of 5 at.%.