CdTe Epitaxial films and their properties

S.N. Maximovsky, I.P. Revocatova, V.M. Salman, M. A. Selezneva, P.N. Lebedeu

► To cite this version:

S.N. Maximovsky, I.P. Revocatova, V.M. Salman, M. A. Selezneva, P.N. Lebedeu. CdTe Epitaxial films and their properties. *Revue de Physique Appliquée*, 1977, 12 (2), pp.161-165. 10.1051/rphysap:01977001202016100 . jpa-00244137

HAL Id: jpa-00244137

<https://hal.science/jpa-00244137>

Submitted on 1 Jan 1977

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

CdTe EPITAXIAL FILMS AND THEIR PROPERTIES

S. N. MAXIMOVSKY, I. P. REVOCATOVA, V. M. SALMAN,
M. A. SELEZNEVA and P. N. LEBEDEV

Physics Institute Leninsky Prospekt 53 Moscow, USSR

Résumé. — Des films de tellure de cadmium ont été préparés par épitaxie par voie gazeuse sur un substrat chauffé par éclairage. Des couches dopées ou non, de type n ou p, présentant les écarts de stoechiométrie souhaités ont pu être obtenues. On présente ici leurs caractéristiques électriques et on discutera les problèmes d'homogénéité des couches. Par ailleurs, des jonctions p-n ont pu être réalisées, leurs propriétés ont été analysées au moyen d'un microscope électronique à balayage.

Abstract. — Undoped and doped CdTe films of p and n type conductivity with a given deviation of film composition from stoichiometry, were grown by a vapour epitaxial technique by heating the substrate with light. Measurement results of electrophysical properties and film homogeneity versus thickness are given. P-N junctions were produced by epitaxy, their properties being investigated with scanning a electron microscope.

The design of reliable CdTe nuclear radiation counters requires the production of p-i-n, p⁺-p, n⁺-n structures. Vapour epitaxy should be the most efficient technique for high-purity and structurally perfect CdTe films taking into account the physical-chemical peculiarities of CdTe.

The present paper is dedicated to the investigation of epitaxial structures grown by a photostimulated vapour epitaxial technique. The following peculiarities should be taken into consideration while producing the above structures :

1) CdTe has an homogeneity range with the limits $\sim 10^{19} \text{ cm}^{-3}$ of excess Cd and Te atoms [1] which determine the electro-physical properties of the films being grown. Due to the above reason epitaxial layer composition should be controlled all through the process of growing.

2) Intensive diffusion of intrinsic point defects and impurities from the film to the substrate and back leads to boundary eroding and broad transition layer formation.

3) High Cd and Te vapour pressure at temperatures exceeding 600 °C results in substrate component evaporation and change in electro-physical properties of both the film and the substrate.

It follows from the above that vapour epitaxy of CdTe should be carried out in a closed volume with a controlled vapour composition. Substrate temperature should not exceed 600 °C and the epitaxial growth rate should be sufficiently high so as to reduce the diffusion process rate between the film and the substrate.

To meet the requirements new devices were developed, their novelty being in the use of an intense light

flux used for substrate surface heating that creates a controlled temperature gradient into the depth of the substrate.

CdTe epitaxial films were grown on substrates of $10 \times 10 \times 0.5 \text{ mm}$ size in ultra-pure hydrogen. The thickness of the film grown was changed from 10 to 800 μm according to growth conditions.

Conductivity type and carrier concentration in CdTe films were defined by C-V dependence measurements of surface-barrier diodes of Hg-CdTe (similarly to Si film measurements in [2]). The measurement technique is based on mercury forming a rectifying contact with CdTe of p and n-type conductivity.

Hg-CdTe contact C-V measurements were carried out with a device where mercury was brought to CdTe film surface along two channels. Channel areas were more than an order different and at carrier concentration calculations the larger channel influence could be neglected. The measurements were carried out at 465 kHz frequency. The carrier concentration n was found from the conventional relation

$$n = \frac{C^3}{(dC/dV) S^2 \epsilon \epsilon_0}$$

where C is the contact capacity, S is the area of a small channel, ϵ and ϵ_0 are the dielectric constants of CdTe and the permittivity of vacuum correspondingly.

For checking the accuracy of the applied technique the carrier concentration and conductivity type of bulk, samples were carried out both by C-V dependence and Hall constant measurements. The obtained data is presented in table I which shows concentration values for one and the same sample obtained by different methods do not differ by more than a factor of 5. The

TABLE I

Samples	Hall measurements concentration	type	mobility	C-V measurements concentration	type
1	4×10^{17}	n	700	2×10^{17}	n
2	4×10^{17}	n	530	9×10^{17}	n
3	3×10^{17}	n	720	9×10^{16}	n
4	2.6×10^{17}	n	227	2×10^{17}	n
5	1.0×10^{17}	n	700	2×10^{16}	n
6	1×10^{16}	n	730	$(3-5) \times 10^{15}$	n
7	6×10^{15}	n	720	3×10^{15}	n
8	7.5×10^{14}	n	750	$(5-10) \times 10^{14}$	n
9	5×10^{14}	n	810	3×10^{14}	n
10	2.6×10^{14}	n		$(4-11) \times 10^{14}$	n
11	2.5×10^{14}	n	1 000	2×10^{14}	n
12	1.2×10^{17}	p	50	3×10^{16}	p
13	5×10^{16}	p	94	5×10^{16}	p
14	3×10^{15}	p	80	2×10^{15}	p
15	6×10^{15}	p	80	2×10^{15}	p
16	4.7×10^{15}	p	25	2×10^{15}	p
17	2×10^{15}	p	37	4×10^{14}	p
18	1.6×10^{15}	p	60	9×10^{14}	p
19	1.3×10^{15}	p	52	5×10^{14}	p
20	4×10^{13}	p	80	2×10^{13}	p

possibility of quick determinations of carrier concentration order through measuring Hg-CdTe contact $C-V$ dependence is confirmed by these results.

Table II shows the carrier concentration and conductivity type measurements of the films grown. It is seen from the table that due to deviation of film composition from stoichiometry without additional doping p and n-type films were obtained with carrier concentration from 1.1×10^{13} to $1.4 \times 10^{17} \text{ cm}^{-3}$ n-type and from 2×10^{14} to $4 \times 10^{16} \text{ cm}^{-3}$ p-type. CdTe charge temperature was 800 °C in all the cases and Cd source temperature varied from 0° to 650 °C. Growing of films doped with In and Cl was also carried out. N-type

films with carrier concentration from 10^{12} to 10^{16} cm^{-3} were obtained.

The measurements of film homogeneity in depth by controlled etching proved that carrier concentration in the film does not essentially change with depth (Fig. 1). However, the transition from n-type film to p-type substrate is rather smooth. This result is in agreement with $C-V$ measurements of epitaxial diodes mentioned below.

By means of the developed technique of CdTe film growing epitaxial diodes were made obtained by In doping an n-type CdTe film growing on to a p-type substrate with a 10^{15} - 10^{16} cm^{-3} hole concentration.

TABLE II

Carrier concentration	Type conductivity	Temperature charge	Temperature Cd	Temperature doped reservoir	Orientation	
4×10^{16}	p	750	0	0	110	
8×10^{14}	p	750	300	0	110	
2×10^{14}	p	750	400	0	110	
1.1×10^{13}	n	750	450	0	110	
2×10^{15}	n	750	500	0	110	
2×10^{16}	n	750	570	0	110	
2×10^{17}	n	750	650	0	110	
10^{12}	n	750	390	135	110	
10^{12}	n	820	520	50	110	
10^{12}	n	810	0	280	110	
10^{12}	n	810	0	300	110	
1×10^{14}	n	820	0	500	110	
2×10^{15}	n	820	0	650	110	
						Cl doped

FIG. 1. — Concentration versus thickness diagram.

Electron concentration in the film amounted to 6×10^{14} – $3 \times 10^{16} \text{ cm}^{-3}$ versus the deviation from stoichiometry. The efforts to obtain p-n junction by vapour pressure change turned out to be fruitless since p substrate changed its conductivity type.

The diode contacts were made by fusing In into n-type films and depositing gold from AuCl_3 on to p-type substrates.

Current voltage characteristics of the obtained diodes are presented in figure 2. They show that cut off voltage

FIG. 2. — Volt-ampere characteristics of diodes. a) A-type diode VAC. Diode surface 3.6 mm^2 . b) A-type diode VAC reverse branches (curve 1), B-type- (curve 2). c) C-type diode VAC. Diode surface 6 mm^2 . In the left upper insets 3 (a) and 3 (b) VAC direct branches are given in semilogarithmic scale.

was 0.7 V, resistance at 0 bias — $10^8 \Omega$ and series resistance $R = 500$ – 3000Ω , much of the latter being due to the high resistance of the p-CdTe-gold contact.

Diode current voltage characteristics under forward bias 0.2–0.7 can be presented as :

$$J = J_0 \exp(q^u/2kT).$$

According to Sah-Noyce-Shockley theory [3] such type of current voltage characteristics corresponds to

the case when the current carrier generation and recombination in the space charge region is the main mechanism of current flowing through the p-n junction. In this case

$$I = \frac{qn_i d}{\tau} \times \frac{kT}{\zeta_0 - eu} \times \exp\left(-\frac{qu}{2kT}\right), \quad [4]$$

where n_i is intrinsic carrier concentration in CdTe ; d is width of space charge layer, $\tau = (\tau_p \cdot \tau_n)^{1/2}$; τ_p and τ_n are hole and electron life time in highly doped material. From capacity measurements

$$d = (2 + 3) \cdot 10^{-4} \text{ cm}.$$

Life time calculated for p-n junctions with In doped n-region (A-type diodes) amounted to 10^{-8} – 10^{-7} s and with Cl doped n-region to $5 \times 10^{-10} \text{ s}$ (B-type diodes). Figure 2(b) gives reverse branches of current voltage characteristics of A-type (curve 1) and B-type (curve 2) diodes. For A-type diodes in a region of high voltage $I \sim V^2$. In B-type diodes at small reverse displacements $I \sim V^2$, and at 2–5 volts a strong current increase is observed. However, the mechanism of reverse current has not been thoroughly studied.

Diode C - V dependences were studied at 8 kHz frequency. At low voltage $V \sim C^{-n}$, where $n=2.5+3$. The data indicates diffuse p-n junction.

At large reverse bias, capacity decreases slower with voltage growth. Similarly to [5] such C - V characteristics can be explained by impurity centres being ionized by electric field.

With the purpose of investigating crystal lattice defects within the spatial charge region of a p-n junction, spectral dependences of short circuit photocurrent were studied. In the impurity region at 300 K the peak with 1.46 eV maximum is observed ; at 78° photocurrent peaks are observed at 1.55 eV and 1.4 eV photon energy. These peaks, evidently, correspond to electron passing from $E_v + 0.05 \text{ eV}$ and $E_v + 0.2 \text{ eV}$ levels to the conductivity band.

Similar peaks in the electroluminescence spectra of epitaxial CdTe diodes were observed in [6].

The cutoff voltage on a number of diodes (C-type diodes) was 0.2 V, zero bias resistance being $10^4 \Omega$ (Fig. 2). The small cutoff voltage and the resistance of these diodes might be connected with carrier tunneling through the crystal lattice defects within the p-n junction space charge region.

The facility of scanning electron microscope was used to measure p-n junction depth as well as its location relative to the film-substrate boundary [8].

The observation of the split surface in the emissive mode of operation reveals the film substrate boundary. On the other hand, the charge collection mode of operation shows the location of the p-n junction. The superimposing of both patterns allows one to see the film-substrate boundary and the p-n junction simultaneously.

Samples of both, A-type (Sample 1) and C-type (Sample 2), were examined. Figure 3 is the micrograph of Sample No. 1 (split normally to the p-n junction). MER-2 device [7] was used to take this micrograph in both modes of operation simultaneously. The micro-

FIG. 3. — Scanning electron micrograph of a sample cleaved normally to the p-n junction (arrows show the film-substrate boundary).

graph displays the junction as a black band. The depth of the junction was 175 μm in Sample No. 1 and 120 μm in the case of Sample No. 2, whereas epitaxial film thickness was 75 and 60 μm correspondingly. The above technique allowed one to reveal microfields caused by eventual inhomogeneity both in the film and on the film-substrate boundary. However, no inhomogeneities of that kind are seen in the micrograph. It proves the high quality of the sample surface preparation before epitaxial film growing. Thus, one can see that intensive diffusion of impurity from the film to the substrate to the depth of 100 to 200 μm takes place in the course of doped epitaxial film growing. It is obvious that such diffusion is far more intensive and, finally, makes it impossible to produce a diode if the film doping comes of composition diversion from stoichiometry.

Excess carrier diffusion length measurements were carried out with the aid of a specially designed attachment to the MS-46 microanalyzer. The short circuit current induced by the electron probe was recorded at 1 μm intervals by scanning normally across the p-n junction with at a speed of 10 $\mu\text{m}/\text{min}$. The electron probe diameter was monitored and did not exceed 0.5 μm in our measurements. The incident beam power was 10^{-6} W to provide a low injection level.

According to a well known theory [6] the current through the junction is :

$$I(x) = I_0 \exp\left(-\frac{x}{L}\right)$$

where x is the distance of the incident beam from the junction ; L is the minority carrier diffusion length. In practice this relation is often violated due to surface

recombination of excess carriers and to the finite range of the beam electrons, i. e. the size of the electron-hole pair source. In our case the error in determination of L did not exceed 20 %. The current maximum position gives the junction depth, i. e. the diffused layer thickness with an accuracy of $\pm 0.5 \mu\text{m}$.

Figure 4 (a, b) shows the curves of $I(x)$ for Samples No. 1 and No. 2. In the case of Sample No. 1 (4a)

FIG. 4. — Charge collection current for short circuit conditions : a) $V_{acc} = 10$ kV, $i_{abs} = 0.1$ nA ; b) $V_{acc} = 15$ kV, $i_{abs} = 0.1$ nA.

the curve $I(x)$ has two maxima ; the distance between them gives the width of the depletion region. We conceived that in this particular case a p-i-n structure was obtained with an i-region width $d = 2.5 \mu\text{m}$. The possibility of i-region width evaluation by an electron-probe technique relates to a probe diameter small compared to d . The maxima on the curve correspond to p-i and i-n junctions which turn out well resolved due to $L_{-p}, L_{-e} > d$ and d greater than electron range that is provided by the selected accelerating voltage of 10 kV. Diffusion lengths for this sample were

$$L_e = 1.4 \pm 0.3 \mu\text{m} ; \quad L_p = 0.9 \pm 0.2 \mu\text{m} .$$

For C-type diodes the width of the depletion region of the junction is less or comparable with probe diameter and so we could not measure it : electron and hole diffusion lengths were

$$L_e = 2.6 \pm 0.5 \mu\text{m} \text{ and } L_p = 1.1 \pm 0.2 \mu\text{m} .$$

The magnitude of the reduced surface recombination velocity $S = 1/LD^{-1}$ was determined from the comparison of the experimental curves with calculated ones [9]. The extension of the electron-hole generation source was taken in account in these calculations. For

the samples of C-type *S* was equal to 5 on the split surface.

The difference in thickness of Sample 1 (A and B-type diodes) and 2 (C-type diodes) p-n junctions can be explained by difference of technological conditions under which they were obtained. Prior to the growth of A and B-type diodes the substrates were strongly etched by an increase in intensity of the light flux.

C-type diodes were grown at a constant intensity of optical heating.

To sum it up, epitaxial CdTe diodes were obtained, the best of them at direct bias have diode characteristics similar to GaAs at the same carrier concentrations in n and p regions [12].

In conclusion the authors wish to thank Academician B. M. Vul for the discussion of the work.

References

- [1] MAXIMOVSKY, S. N. *et al.*, Proceeding of the International Symposium on Cadmium Telluride, June 29-30, 1971, p. XII.
  - [2] PONOMAREV, A., *Electronical Technics* USSR, 1969, ser. 2 No. 5, p. 45, 8.
  - [3] SAH, R. S., NOYSE, R. N., SHOCKLEY, W., *Proceeding S. R. E.* **45** (1957) 1228.
  - [4] PYKUS, G. E. « Origin of semiconductor devices theory », USSR, Nauka 1965, p. 191.
  - [5] KALUGINA, L. I., UHTANOV, E. G., KIREEV, P. S., *Radio-technics and Electronics* **15** (1970) 2623.
  - [6] SHOCKLEY, W., PEARSON, G. L., HYNES, I. R., *Bell. System Techn.* **28** (1949) 334.
  - [7] FETISOV, D. V., KUSHNIR, U. M., POSTNIKOV, B. B., *Reports of A. N. USSR ser. Phys.*, XXXVI, p. 1861 (1972).
  - [8] SPIVAK, G. V., SAPARIN, G. B., BIKOV, M. V., *Usp. Fiz. Nauk.* **99** (1969) 635.
  - [9] SELEZNEVA, M. A., KUPREJANOVA, T. A., DIZMAN, S. A., *Short Physical Reports* 1975, No. 10, p. 45.
  - [10] SELEZNEVA, M. A., PHYLIPPOV, S. S., Preprint of Applied Mathematics Institute AN USSR, 1975, No. 38 and No. 60.
-