Bulgarian Chemical Communications, Volume 48, Special Issue E (pp. 378 - 383) 2016

Mathematical modelling concerning the influence of chemical composition upon hardness of cadmium telluride crystal

- Part 1-

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Cadmium telluride is an alloy with semiconductor properties obtained by melting on furnaces of cadmium and tellurium, and is currently the basic material for manufacturing photovoltaic cells. The mathematical model developed in this paper expresses the hardness values of cadmium telluride crystal, depending on the micro-alloying elements. This material has been studied in the literature only in terms of properties defining characteristics of semiconductors, without presenting any data concerning the influence of micro-alloying elements upon hardness values. Micro-alloying elements concentration was determined using laser ablation technique with New Wave Research UP213 coupled to an ICP-MS Agilent 7500 and hardness values were determined with DUH-211S Shimadzu ultra-micro hardness tester, the Martens method. The mathematical model is aimed to determine hardness of cadmium telluride crystals depending on the chemical composition.

Keywords: hardness, laser ablation, alloy, hardness tester

INTRODUCTION

Cadmium telluride is an alloy with semiconductor properties, obtained through melting in special furnaces tellurium and cadmium semimetals and is currently the base material for manufacturing photovoltaic cells. Furthermore, through micro-alloying (crystal doping) with mercury, the base material for high performance infrared detectors used in spectrometry and remote sensing is manufactured, whereas through micro-alloying with zinc is obtained the base material for manufacturing Röntgen and Gamma detectors [1, 2].

Cadmium telluride is characterized through a crystal, hence fragile structure. In the process of manufacturing large areas solar panels, the cadmium telluride, as base material, should provide corresponding mechanical characteristics depending on operating conditions. That is why a thorough study and an advanced characterization of the mechanical behavior of cadmium telluride crystal could be extremely useful.

The paper proposes a mathematical model which provides the hardness values of cadmium telluride crystal depending on the micro alloying elements. This material has been studied in the literature only in terms of defining the characteristics of semiconductor properties [3, 4, 5, 6, 7], without presenting any data concerning the influence of micro-alloying elements upon hardness values. That is why, providing a model and, consequently, having the possibility to predict the mechanical behavior and especially the hardness of cadmium telluride is of the last importance for practical issues depending on operating particularities.

EQUIPMENT USED FOR THE ACQUISITION OF EXPERIMENTAL DATA

LA-ICP-MS technique is particularly useful for in situ samples analyzes, that is, for applications that require understanding of elementary spatial variation for the sample.

Laser ablation (*LA*) coupled to an ICP-MS equipment (mass spectrometry with inductively coupled plasma) may perform direct analysis on almost all materials.

This technology was used in determining the composition of cadmium telluride crystal, by the instrumentality of a LA model UP213 of New Wave Research Company, coupled with a model Agilent 7500 ICP-MS, Agilent Technologies, from the laboratory of Instrumental Analysis of the Faculty of Food Engineering, University of Suceava Romania (Fig.1). The UP 213 (213 nm laser ablation) releases atomic vapors of the material absorbed in the ICP MS to quantitatively determine its elements.

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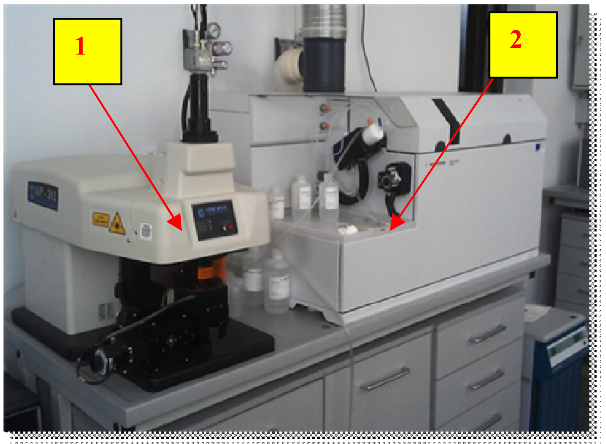

Fig.1. Laser ablation system UP-213 New Wave (1) – ICP-MS Agilent 7500 (2)

The UP series of laser ablation equipment manufactured by New Wave Research Company is specially designed to work with *ICP-MS* and *ICP-OE* systems. The *YAG* laser of *UP213* ablation equipment is operating in *213 nm UV* region, Fig.2.

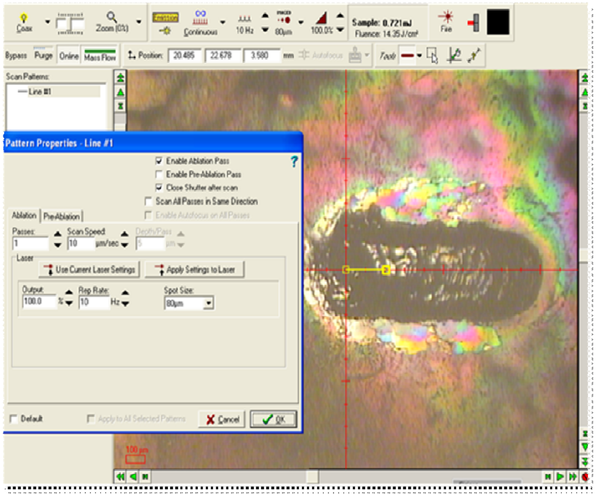

Fig.2. Ablation zone on surface CdTe crystal after a qualitative and quantitative analysis performed with NewWave UP213 spectrometer coupled to an Agilent 7500 ICP-MS; laser continuously 10Hz rate, scan speed 10 μm/s, working energy 0.721 mJ channel length 1 mm

Using ICP MS type spectroscopy to study hardness allows highlighting the influence of micro alloying elements traces upon the hardness.

Micro hardness of cadmium telluride crystal was investigated and evaluated using the Shimadzu DUH-211S micro hardness tester (Fig.3).

RESULTS

In this experimental research, cadmium telluride single crystal has the composition, concentrations of components and mechanical characteristics consistent with those presented in Tables 1 and 2 and determined by ICP-MS-LA technique. Moreover, the research was focused also on the distribution of the segregation of chemical elements of micro alloying with respect to the geometrical position of a point down the axis of the crystal, distribution enabling further correlation of the composition and concentration with the semiconductor, mechanical and thermal properties of cadmium telluride. To this end cadmium telluride crystal was mechanically cut lengthwise and on the symmetry axis have been marked distances of 5 mm on 5 mm (17 areas,), Fig.4.

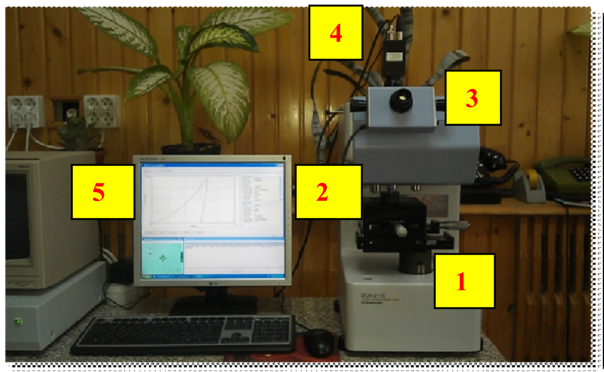

Fig.3. Shimadzu DUH-211S micro hardness tester (1), sample manual positioning system (2), footprint optical viewing system (3) image pickup video system CCD (4), hardness measurement and footprint inspection software (5)

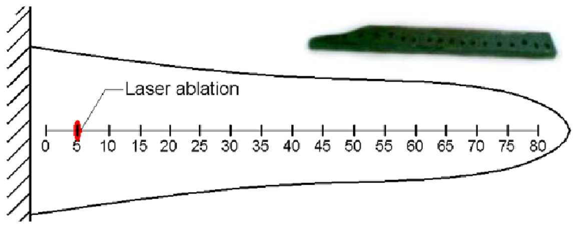

Fig.4. Analysis scheme on areas of cadmium telluride crystal, [8], [11]

The analysis of the distribution of micro alloying elements of cadmium telluride crystal on was extended to all ten chemical elements, whose average concentration (mean concentrations of all the seventeen measurement areas) is shown in Table 1.

Determination of the mechanical characteristics (HMV, HM - Martens hardness), indentation elasticity modulus (E_{IT}), tendency of creep indentation (C_{IT}) and depth of indentation for cadmium telluride crystal depending on the micro alloying elements for the 17 analyzed areas (S1-S16) was instrumented through the Martens method for determining hardness, using an automatic hardness testing device Shimadzu DUH-211S, (n_{it}=plastic and elastic portions of indentation work).

Table 1. Average concentrations of micro alloying elements in a cadmium tellurium single crystal (ppb=parts per billion)

Test no.	V(ppb)	Cr(ppb)	Co(ppb)	Ni(ppb)	Cu(ppb)
0	120	334	29	37	31
1	120	250	28	36	30
2	130	220	27	33	33
3	150	210	25	25	35
4	154	180	24	25	36
5	154	168	24	24	37
6	159	165	25	24	38
7	161	163	24	24	40
8	161	155	24	23	42
9	168	148	25	22	44
10	170	134	26	21	48
11	171	132	25	20	49
12	173	129	25	19	50
13	180	127	24	19	53
14	220	125	24	19	58
15	221	125	23	18	60
16	229	124	22	18	61
$\bar{x}$	167,117	169,941	24,941	23,941	43,823
stdev	31,966	56,302	1,748	5,984	10,107

Table 1. Continuation

Test no	Zn(ppb)	Sn(ppb)	W(ppb)	Tl(ppb)	Pb(ppb)
0	5100	3,4	46	0,21	0,57
1	3800	3,8	33	0,21	0,51
2	2500	3,9	25	0,18	0,35
3	1800	5	19	0,19	0,41
4	1660	9,5	17	0,21	0,37
5	1610	9,4	18	0,22	0,44
6	1590	8,6	20	0,2	0,45
7	1580	9,2	18	0,25	0,43
8	1570	9,6	17	0,17	0,54
9	1550	9,6	20	0,16	0,42
10	1420	9,5	17	0,2	0,41
11	1419	9,5	15	0,15	0,46
12	1411	9,4	13	0,19	0,71
13	1405	9,4	12	0,16	0,57
14	1400	9,3	11	0,18	0,44
15	1398	9,2	11	0,18	0,33
16	1398	9,4	11	0,14	0,47
$\bar{x}$	1918,294	8,10	19,00	0,188	0,463
stdev	1015,069	2,359	8,909	0,027	0,093

Table 2. Mechanical characteristics of CdTe Crystal depending on the micro alloying elements of the 17 areas of analysis

Cr. no.	F_{max} [mN]	h_{max} [µm]	HMV [N/mm^2]	HM_s [N/mm^2]	Analyzed area
1	500.50	51.985	697.33	538.897	S 0
2	500.12	52.587	681.33	526.533	S 1
3	500.71	52.850	679.33	524.987	S 2
4	500.50	53.046	674.33	521.123	S 3
5	500.91	53.431	667.66	515.97	S 4
6	500.21	53.544	663.66	512.88	S 5
7	500.50	53.554	662.66	512.10	S 6
8	500.10	53.644	661.33	511.07	S 7
9	500.50	53.731	660.66	510.56	S 8
10	500.98	53.723	657.33	507.98	S 9
11	500.00	53.750	649.33	501.80	S 10
12	500.10	53.815	649.00	501.54	S 11
13	500.50	53.809	644.33	497.93	S 12
14	500.50	53.815	640.66	495.10	S 13
15	500.50	54.001	639.66	494.33	S 14
16	500.50	54.194	638.66	493.56	S 15
17	500.03	54.256	635.00	490.72	S 16

Table 2. Mechanical characteristics of CdTe Crystal depending on the micro alloying elements of the 17 areas of analysis (continuation)

Cr no.	Hit [N/mm^2]	Eit [N/mm^2]	Cit [%]	nit [%]	Analyzed area
1	898.167	3.096e+004*	0.624	15.825	S 0
2	881.805	3.032e+004*	0.621	16.265	S 1
3	872.484	2.982e+004*	0.596	16.425	S 2
4	864.408	2.640e+004*	0.590	16.434	S 3
5	860.234	2.617e+004*	0.588	16.486	S 4
6	860.758	2.601e+004*	0.587	17.236	S 5
7	854.355	2.504e+004*	0.530	17.373	S 6
8	853.564	2.500e+004*	0.529	17.397	S 7
9	848.605	2.499e+004*	0.529	17.498	S 8
10	837.764	2.498e+004*	0.524	17.514	S 9
11	837.764	2.489e+004*	0.524	17.914	S 10
12	827.154	2.489e+004*	0.518	17.936	S 11
13	824.842	2.487e+004*	0.506	18.079	S 12
14	823.154	2.484e+004*	0.504	18.116	S 13
15	821.792	2.483+004*	0.504	18.129	S 14
16	820.304	2.479e+004*	0.503	18.257	S 15
17	819.602	2.479e+004*	0.502	18.568	S 16

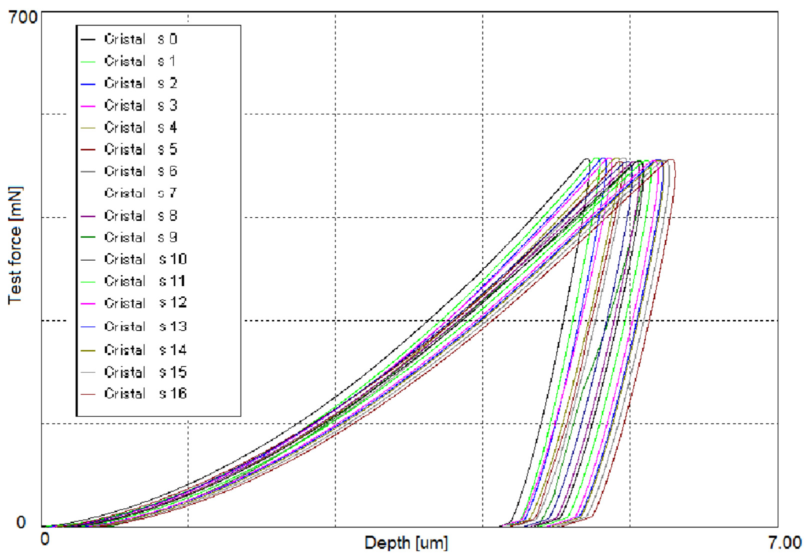

Fig.5. The graphical representation of the evolution of average hardness of cadmium telluride crystal depending on the micro alloying elements for the 17 analyzed areas: power (F) - indentation depth (h_{max}), Martens Hardness Test, using hardness testing device Shimadzu DUH-211S

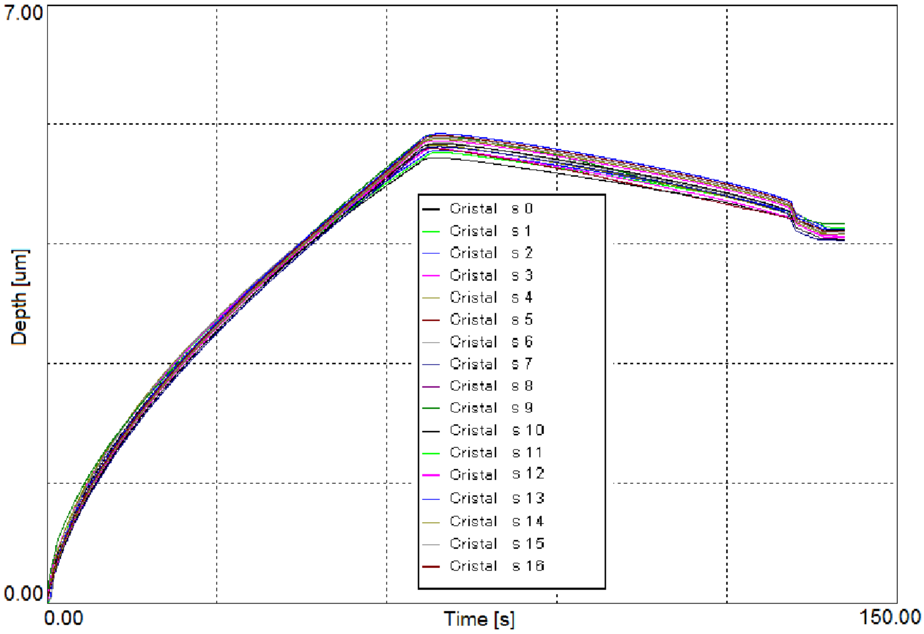

Fig.6. The graphical representation of the evolution of average hardness of cadmium telluride crystal depending on the micro alloying elements for the 17 analyzed areas: indentation depth (h_{max}) – time (t), Martens Hardness Test, using hardness testing device Shimadzu DUH-211S

Also plotted in Fig.5 it is shown the evolution of the indentation force (F) depending on the indentation depth (h) of the indenter, respectively in Fig.6 the variation of the indentation depth (h) of the indenter in time, for the cadmium telluride crystal.

CHECKING THE HOMOGENEITY OF HARDNESS VALUES VARIANCES FOR CADMIUM TELLURIDE CRYSTAL

Checking the homogeneity of hardness values variances for cadmium telluride crystal is performed using Bartlett Test and finally verifying χ^2_B which should obey to the law χ^2 with *k-1* degrees of freedom. The decision concerning *H_0 hypothesis* will be accepted if: $\chi^2_B \le \chi^2_{\nu;\alpha} = \chi^2_{k-1;\alpha}$, and rejected if: $\chi^2_B \rangle \chi^2_{\nu;\alpha} = \chi^2_{k-1;\alpha}$ [9, 10].

Table 3. Bartlett test results for CdTe crystal hardness values

Current no.	Bartlett parameters checking	Crystal area								
		Area 0	Area 1	Area 2	Area 3	Area 4	Area 5	Area 6	Area 7	Area 8
1	k- area no.					17				
2	n_i – sample	3	3	3	3	3	3	3	3	3
3	$\nu_i = n_i - 1$	2	2	2	2	2	2	2	2	2
4	s^2 (variance)	0,33	12,33	20,33	9,33	6,33	20,33	2,33	6,33	4,33
5	$\nu_i \cdot ln\, s^2$	-2,217	5,024	6,024	4,466	3,690	6,024	1,691	3,690	2,931
6	$\nu \cdot ln\, s^2$					68,59724				
7	$\sum_{i=1}^{k} \nu_i \cdot ln\, s_i^2$					47,96952				
8	$\frac{1}{3(k-1)}$					0,02083				
9	$\sum_{i=1}^{k} \left(\frac{1}{\nu_i} - \frac{1}{\nu} \right)$					8,00003				
10	χ^2_B **- calculated**					**17,68**				
11	χ^2_B **- table**					**27,58**				

Table 3. Bartlett test results for CdTe crystal hardness values (continuation)

Current no.	Bartlett parameters checking	Crystal area							
		Area 9	Area 10	Area 11	Area 12	Area 13	Area 14	Area 15	Area 16
1	K- nr. area no.	17							
2	n_i - sample	3	3	3	3	3	3	3	3
3	$\nu_i = n_i - 1$	2	2	2	2	2	2	2	2
4	s^2 (variance)	0,33	6,33	13	12,33	9,33	1,33	0,33	3
5	$\nu_i \cdot ln\, s^2$	-2,217	3,690	5,129	5,024	4,466	0,570	-2,217	2,197
6	$\nu \cdot ln\, s^2$	68,59724							
7	$\sum_{i=1}^{k} \nu_i \cdot ln\, s_i^2$	47,96952							
8	$\frac{1}{3(k-1)}$	0,02083							
9	$\sum_{i=1}^{k} \left(\frac{1}{\nu_i} - \frac{1}{\nu} \right)$	8,00003							
10	χ_B^2 **- calculated**	**17,68**							
11	χ_B^2 **- table**	**27,58**							

According to the results shown in Table 3 with respect to checking the homogeneity of variance for hardness values recorded for the CdTe crystal: $\chi^2_{B\text{-}calculated}$ = **(17,68)** < $\chi^2_{B\text{-}table}$ **(27,58)**. Consequently the hypothesis of the homogeneity of hardness dispersions should be accepted, with a probability $P = 1 - \alpha = 1 - 0,05 = 0,95 = 95\%$.

It is clear that using Bartlett test, the results concerning the influence of micro alloying elements upon the hardness obtained for cadmium telluride crystal is confirmed by 95% confidence level.

CONCLUSIONS

In order to establish a link between the micro alloying elements and cadmium telluride crystal hardness experimental researches were carried out using ablation laser equipment UP213 New Wave Research, coupled to ICP-MS 750 Agilent, respectively Martens method for hardness measuring with hardness testing device Shimadzu DUH-211S.

Moreover, using the method of homogeneity of hardness values variance (Bartlett test) was checked and validated by 95% confidence level, the influence of micro alloying elements upon cadmium telluride crystal hardness.

According to the theoretical and experimental research, as shown from both Figures 5, 6 and values in Tables 1, 2, it is obvious that the influence of micro alloying elements have a significant role on the mechanical characteristics of cadmium telluride crystals.

In order to extend the current research a mathematical model able to predict the value of cadmium telluride crystals hardness depending on the micro alloying elements should be developed. This model will be drawn up based on the values of the alloying elements in Table 1, with hardness values specific to the analysis of the crystal according to Table 2.

The results of Bartlett test on the values determinated and presented in this paper encourage us to continue the work through developing the mathematical model for predicting the influence of chemical composition upon hardness of cadmium telluride crystal.

ACKNOWLEDGEMENTS

Financial support from the POSCCE project “Centru integrat de cercetare, dezvoltare si inovare pentru materiale Avansate, Nanotehnologii si Sisteme distribuite de fabricatie si control (MANSiD)”, Contract No. 671/09.04.2015 is acknowledged.

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