Multitarget system for growth of thin films by pulsed laser deposition

M. Herrera,[1,*] R. Castro-Rodríguez,[1] O. Gómez,[1] V. Rejón,[1] P. Bartolo-Pérez,[1] S. Barkun,[2]
A. Martel,[2,3] and J.L. Peña[1,3]
[1]*Departamento de Física Aplicada, Centro de Investigación y de Estudios Avanzados*
Instituto Politécnico Nacional, Unidad Mérida
Apartado postal 73, Cordemex, 97310 Mérida, Yuc., Mexico
*e-mail: *mherrera@mda.cinvestav.mx.*
[2] *Facultad de Física, Universidad de La Habana*
San Lázaro y L. Vedado, 10400 La Habana, Cuba
[3] *Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada, Instituto Politécnico Nacional*
Altamira, Km. 14.5, Carretera Tampico-Puerto Industrial Altamira
Apartado postal 165, 89600 Altamira, Tamps., Mexico

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In this work we present the design, construction and the evaluation of a system to growth multiple layers of thin films using the pulsed laser deposition (PLD). The system is equipped with a mechanism of multiple targets and substrates. It has two revolving plates that can be manipulated from outside the chamber. The first serves to interchange four targets without breaking the vacuum or altering the internal conditions of the chamber. It also allows to put to the target in rotation around it's own axis. This rotation gives uniformity to the wearing down of the target thus enhancing the uniformity of the growing film. The second plate allows to change the substrate without opening the vacuum chamber. This second plate has three substrate holders. The system has a substrate heather that works at a maximum temperature of 600°C. Both mechanisms are mounted in individual standard 6 inches ConFlat flanges and can be used in cameras of high or ultrahigh vacuum. The working chamber is evacuated by a standard oil diffusion pumping system. A Nd:YAG (Neodymium Yttrium Aluminum Garnet) infrared laser at wavelength of 1064 nm and about 25 Wcm^2/pulse is used to vaporize the target. The capability of the system is evaluated by growing several basic structures of super-stratum CdTe-CdS used for solar cell on conductive glass (TCO): TCO/CdS, TCO/CdTe and TCO/CdS/CdTe and characterizing them by grazing incidence X-ray diffraction (GIXRD).

Keywords: Pulsed laser deposition; CdS films; X-ray analysis

En este trabajo se presenta el diseño, construcción y evaluación de un sistema de crecimiento de películas delgadas de capas múltiples usando el depósito por láser pulsado. El sistema está equipado con mecanismos de blancos y substratos múltiples que son manipulados desde el exterior de la cámara. El primero sirve para cambiar el material (blanco) que se va a depositar sin alterar el vacío interno de la cámara. Éste tiene capacidad para cuatro blancos y permite la rotación de uno de ellos sobre su propio eje para ser irradiado por el láser, obteniéndose uniformidad en el crecimiento. El segundo sirve para cambiar los substratos sin abrir la cámara, mediante un mecanismo que permite ubicar desde fuera de la cámara, sin perder vacío, el substrato que va ser utilizado. Este mecanismo se acopla a un calentador de substratos que puede operar hasta 600°C. Ambos mecanismos son montados en bridas de 6 pulgadas tipo ConFlat y pueden ser utilizados en cámaras de alto o ultra alto vacío. La cámara de trabajo es evacuada por un sistema con una bomba de difusión de aceite. Se utiliza un láser infrarrojo de Nd:YAG (Neodymium Yttrium Aluminum Garnet) con una longitud de onda de 1064 nm y 25 Wcm^2/pulso. El sistema es evaluado mediante el crecimiento de estructuras de CdTe-CdS sobre vidrio conductor (TCO): TCO/CdS, TCO/CdTe y TCO/CdS/CdTe, utilizadas para celdas solares. Estas estructuras son caracterizadas por difracción de rayos X rasantes.

Descriptores: Depósito por láser pulsado; películas de CdS; análisis de rayos X

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1. Introduction

The high kinetic energy of particles, due to the absorption of the laser radiation by the target material, allows the pulsed laser deposition (PLD) technique to deposit thin films with structural and stoichiometric properties similar to those that require a special processing after growing the material [1].

Using this technique we can obtain a great diversity of materials: superconductors, semiconductors, ferroelectrics, biomaterials, etc. [2]. In addition, the facility to control the process parameters makes of this technique one of most viable means for the preparation of structures with multiple layers. As an example can be mentioned the photovoltaic cells of super-stratum type [2].

In order to obtain structures with multiple layers is necessary to evaporate films from different material on the same substrate. To do this it is required to have tablets of the materials to be evaporated (targets) within the vacuum chamber and to be able to interchanging them at the suitable moment without breaking the hermeticism of the system. This is possible only if the system has a mechanism for target changing that at the same time allows uniform rotation of the target during the laser ablation [2]. On the other hand, the growth of the thin films by PLD requires a process that guarantees the control of such parameters as the pressure in the chamber, the cleanness of its internal parts, the temperature of the substrate and the amount of laser pulses to be delivered.

The contact with the atmosphere of a just obtained film can allow an undesirable oxide formation on the film surface, these oxides would remain as impurities in a multilayer structure. For this reason, to grow another film in a single stage system, it is necessary to wait until the temperature falls below $50°$C to avoid high temperature oxidation or some other physical change when exposing the film to the atmosphere. That implies that the performance and possibilities of a system increases if besides the mechanism for target changing, the system possesses a mechanism for substrate changing in one vacuum cycle.

2. Experimental details

2.1. Target manipulator

The design of the target manipulator mechanism has to satisfy the following requirements [3]

a) Provides the system with a revolving plate that allows changing targets without breaking the vacuum or varying the internal conditions of the chamber.

b) Allows the rotation of the target around its own axis, that increases the uniformity of the wearing down or erosion of the target that consequently enhances the uniformity of the film growth.

c) Allows handling the mechanism from outside the vacuum chamber.

d) Protects the other targets during the incidence of the laser.

e) Permits to place the target in the corresponding holder without difficulty.

Figure 1 shows the mechanism that allows the target to rotate and to be manipulated from outside. The knob (1) is pushed to shift to another target. The knob is hold to the axis of a vacuum rotary seal (2), which allows up-down and rotatory movements. The knob travels around until other target is in the suitable position. When doing this operation we perform the following steps: pressing the knob (1) the axis is introduced and a gear (3a), mounted in this axis, pushes a stainless steel bushing (4) in which an element (5) of a 3 bar coupler is flatted. When the element (5) moves, it transmits the movement to the element (6) which has a groove that allows to slide between two screws that are in another stainless steel bushing (7) and thus to be able to transmit movement to the element (8).

The element (8) is a connector which puts the target in rotation and is united to the element (6) by means of a stainless steel bearing to allow its rotation without interfering with its mobility. This connector has in one of its ends a pin to be able to slide in another aluminum ring (9) that is grooved and has a bushing of Teflon. The ring (9) is supported for the axis of

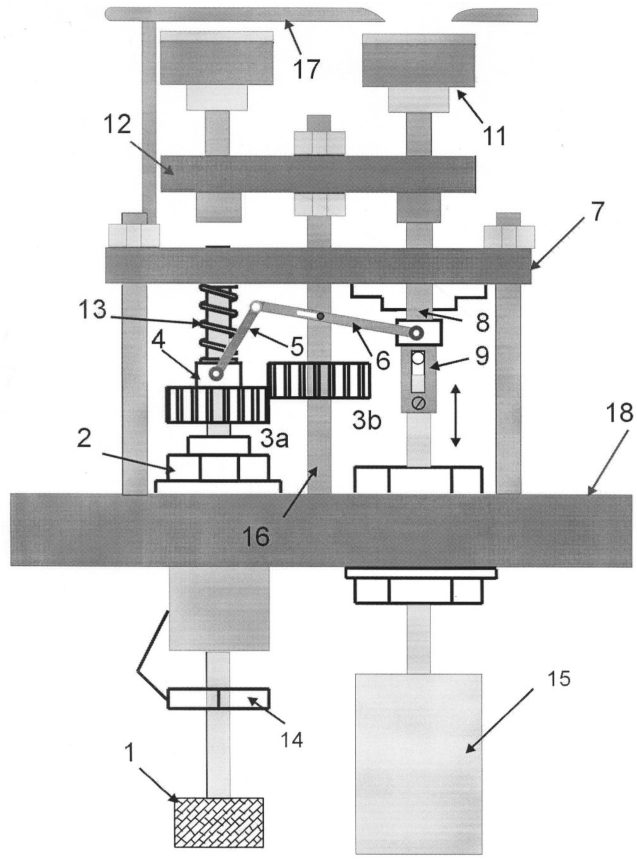

FIGURE 1. Design details of the target manipulator mechanism.

another rotatory seal (10) witch is coupled to a motor at the outside of the chamber. When the connector (8) is moved, it disengages from the lower part of the target holder (11), mounted in a rotatory disk (12). Once the connector (8) is disengaged from the target holder, is necessary to revolve the goatee (1) so that the gear (3a) transmits movement to the (3b) one witch puts the disk (12) in rotation and them allow selecting another target. Upon leaving of pushing the goatee (1), the spring (13) returns back the bushing (4) and the connector (8) is coupled again to the target holder. Lastly, the motion of the motor (15), connected to the rotatory seal (10), will put the target holder in rotation.

Figure 1 shows that rotatory seals (2) and (10) and the axis (16) are housed in a standard Conflat flange of 152.4 mm diameter (18). The rigidity of the mechanism as well as the subjection of the parts is provided for the platform and four posts fixed in the flange (only two of them are shown in the Figure). The shield (17) fastened by means of two screwed to the platform posts, acts as shutter to the rest of the targets.

2.2. Substrate manipulator

In PLD technique of thin film deposition, to clip the substrate to the holder, as well as the relative position substrate-target, are important parameters. Frequently the substrate is warmed up to obtain a good adhesion and/or epitaxial growing of the target material. For many of the target materials the substrate heating offers a good uniformity. Sometimes in this process an oxygenated atmosphere and temperatures above $600°$C are utilized.

Usually, the substrate is placed in front of the target and the distance between them depends on many factors. The most significant of them is the energy remitted by the target. At pressure of 35 mTorr and laser energy density of 4 Jcm^2, the length of the "pen" is approximately of 5.5 cm. When the distance is smaller there is not great difference in the size of the ejected particles, but when this distance is greater, the proportion of small particles decreases. The ability to fit this distance is an important parameter in the PLD design. In more sophisticated applications it can be necessary to move the substrate laterally.

When the films are deposited without substrate heating, it is only required a mechanism that allows to locate the substrate in front of the target. If the substrate is warmed up to relative high temperature ($\sim 600°$C) in an oxidizing atmosphere, the substrate holder necessary is more complex. The conventional spiral heaters from nicromel wire are a good laboratory option for heating in this case. Another choice is to use the radiation produced by quartz bulb lamps that is cleaner.

In this system is important to allocate a place for the vacuum seals that allow the connections of the electrical energy for the heater and thermocouples. The necessity to have a uniform substrate temperature entails the use of a holder of a suitable thickness made of a material that conserves the calorific energy and not allows abrupt changes of temperature.

Figure 2 shows the mechanism that allows manipulating the substrate holder, thermocouple and heather. In order to be able to place in the suitable position, and later to make the change of the substrate holder, it is necessary to rotate the knob, that is holds to the axis of the rotatory vacuum seal (1). At an other end of this axis, at inner part of the flange (2), is placed a gear (3), which connected to another gear, placed in axis (4) at witch the substrate holders are mounted. The last gear is located between the flange (2) and the board of support of the substrate holder (5) and transmits the movement to axis (4) and them allow the positioning of the substrate holder.

The suitable position of the furnace (8) is obtained by means of rotation and displacement of another knob, placed in axis (6) of the vacuum seal (7). The correct positioning of the thermocouple (10) is obtained similarly by rotatory and axial movement of the third knob at outside end of axis (9). The three vacuum seals and all mechanism are mounted in the 6 inches ConFlat flange (2). Last is the piece that separates the internal part of the chamber at the outside.

2.3. Film preparation

For the deposition of the films by PLD, a pulsed Nd:YAG infrared laser was used. The laser is operating at 1064 nm,

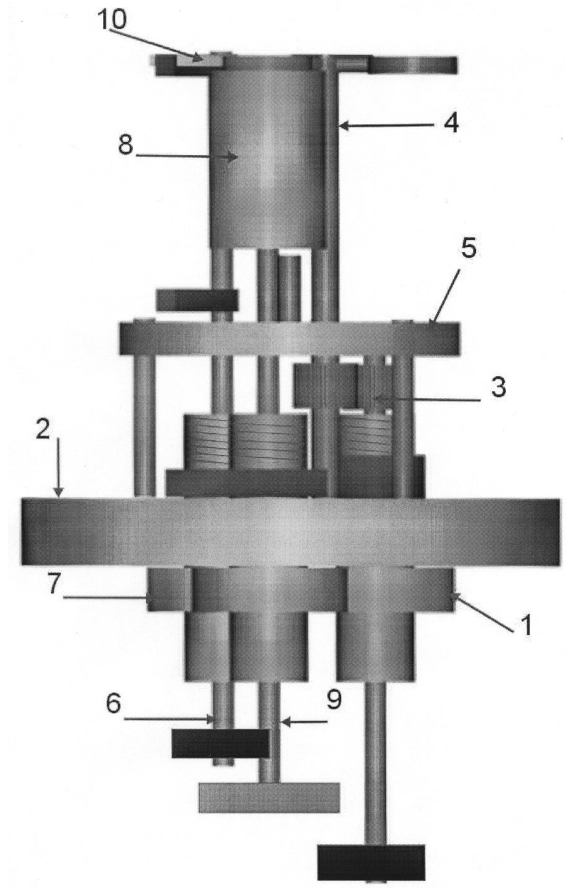

FIGURE 2. Schematic of the substrate holder manipulator.

repetition rate of 5 Hz and pulse width of 10 ns. The laser fluency was optimized at about 25 Jcm^2. The laser is focused by a 20 mm focal length to spot size of approximately 0.002 cm^2.

A 3 mm thickness and 15 mm diameter CdS tablet was utilized as CdS target. This tablet was pressed from 99.999% purity CdS powder from Cerac. The CdTe target, of similar thickness and diameter, was prepared by vacuum evaporation of 99.999% purity CdTe powder from Cerac. The Auger and X-ray analysis have showed that this target has the CdTe stoichiometry and [111] preferential orientation. During the growth the target was set in rotation at 30 rpm. The film growing was carried out at 5×10^{-5} Torr. In order to clean the target surface before the deposition it was erosioned by 75 laser pulses. The film thickness was controlled by means of the total quantity of laser pulses and the target-substrate separation.

Three types of film were grown using the PLD technique for the evaluation of the system: ITO/CdS, ITO/CdTe and ITO/CdS/CdTes. The first two films are compared with similarly films grown by close-spaced vapor transport (CSVT) technique. The film growing conditions are summarized in Table I. The P04-PLD is an ITO/CdS/CdTe structure, specially grown by the PLD technique in one vacuum cycle without opening the chamber. It has very thin layers of CdS and CdTe.

TABLE I. Film growing conditions.

Film	Kind of structure	Substrate temperature (°C)		Target-substrate separation (mm)		Number of pulses	
PLD							
		CdS	CdTe	CdS	CdTe	CdS	CdTe
P01-PLD	ITO/CdTe	—	200	—	30	—	20 000
P02-PLD	ITO/CdS	400	—	50	—	5 000	—
P03-PLD	ITO/CdS/CdTe	400	200	50	30	5 000	20 000
P04-PLD	ITO/CdS/CdTe	200	200	50	30	2 500	2 500
CSVT							
Film	Kind of structure	Substrate temperature (°C)		Source temperature (°C)		Deposition time (min)	
		CdS	CdTe	CdS	CdTe	CdS	CdTe
C01-CSS	ITO/CdTe	—	575	—	450	—	2
C01-CSS	ITO/CdS	650	—	450	—	2	—

2.4. Film characterization

Chemical composition of target and structure were analyzed by Auger electron spectroscopy (AES) with ESCA-SAM Perkin Elmer 560 model, equipped with a double pass cylindrical mirror analyzer, with a base pressure of 10^{-9} Torr. AES spectra of CdS and CdTe targets were obtained with a 3 keV electron beam with typically 0.2 μA current incident at 45 to the surface normal in the differential mode. Cleaning of targets and AES profile of the structure were obtained with an Ar^{+} beam with energy of 4 keV and a current density of 0.36 μA/cm^2.

3. Results and discussion

3.1. Mechanical results

The design and construction of the target manipulator mechanism allowed to carry out the exchange and the rotation of targets in a simple and rapid manner: the mechanism is relatively small and can take targets up to 25.4 mm diameter, that can be mechanical affix on the holder.

The design and the construction of the substrate manipulator mechanism allowed the outer manipulation of the substrates the thermocouple and the furnace in a fast and simple way, without having to break the vacuum in the chamber. The above mentioned mechanism allowed to prepare structures of multiple layers and to provide adequate in situ heat treatment of these structures.

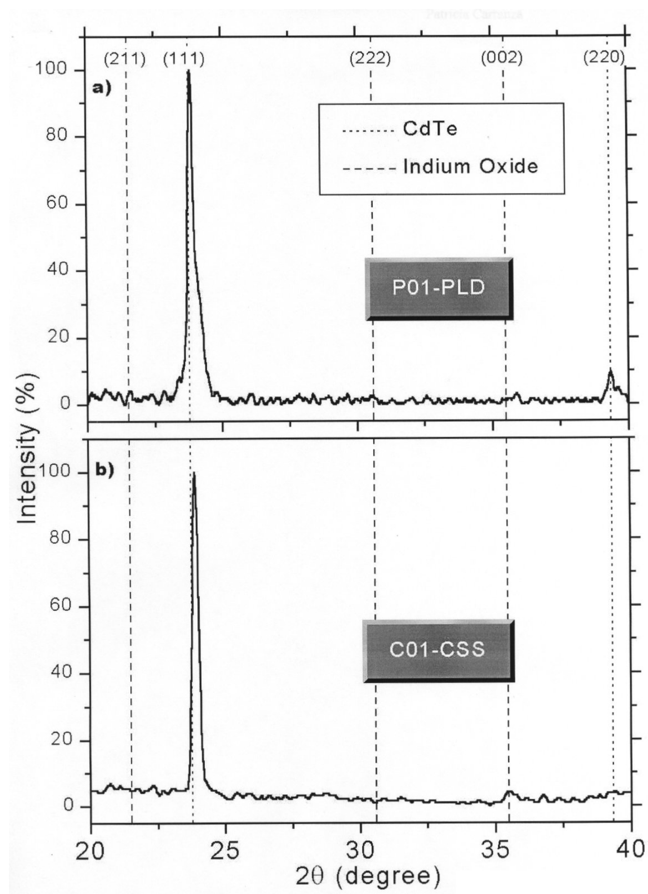

FIGURE 3. GIXRD patterns of Glass/ITO/CdTe structures at $0.4°$ X-ray incidence angle with the PLD technique (upper figure) and CSVT technique (lower figure).

3.2. Film results

Figure 3 shows the smoothed and normalized GIXRD diffraction patterns, under $0.4°$ of X-ray incidence, of the ITO/CdTe layers. As can be appreciated in Fig. 3 (upper) the PLD system produces CdTe films with the preferential texture in the [111] direction. This direction is typical of the layers of ITO/CdTe done by CSVT, as it is possible to be appreciated in Fig. 3 (lower) and have been reported by other authors, Cruz *et al.* [6], who used the stacked elemental layer (SEL) technique, Paulson *et al.* [7], who used CSVT. In our CdTe PLD films, the [111] peak is deformed with respect to homologous of the CSVT film. This can be due of a greater degree of stress of the superficial layers of this film, because

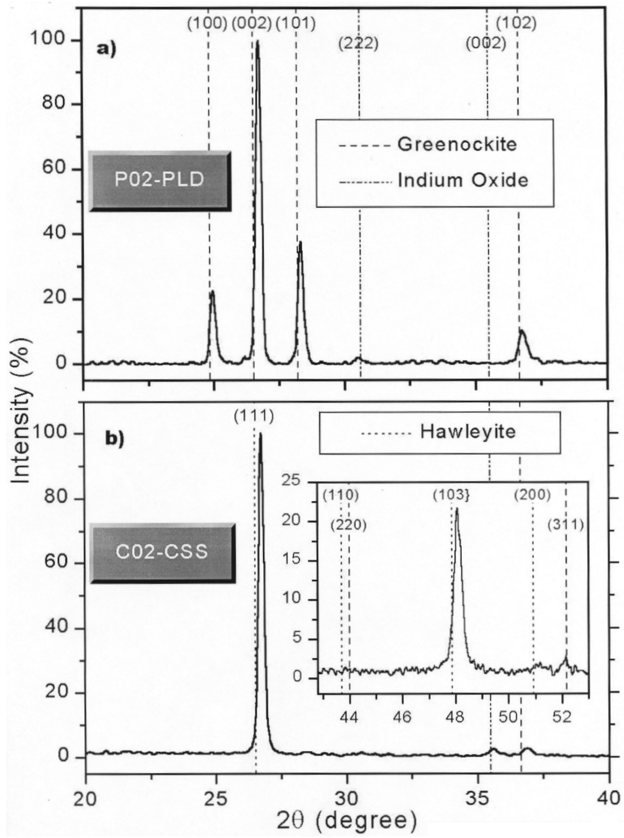

FIGURE 4. GIXRD patterns of Glass/ITO/CdS structures at 0.4° X-ray incidence angle with the PLD technique (upper figure) and CSVT technique (lower figure).

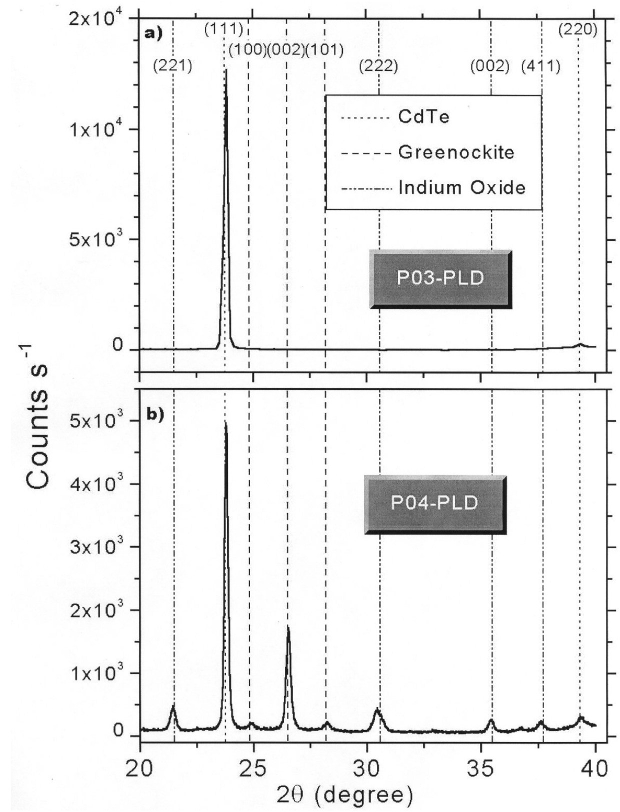

FIGURE 5. GIXRD patterns of Glass/ITO/CdS/CdTe structures at 0.3° X-ray incidence angle for thick film (upper figure) and thin film (lower figure).

the temperature of growth is 250°C smaller than in the case of the CSVT. It in our experimental conditions it was not possible to grow CdTe films at temperatures of about $400-450^\circ$C, due to very low deposition rate at this temperature.

Figure 4 shows the smoothed and normalized GIXRD diffraction patterns, under 0.4°C of incidence, of the ITO/CdS films. As can be seen in Fig. 4 (upper), the PLD system produces CdS films with hexagonal greenockite like structure and preferred orientation along [001] direction and wheel definite [100] and [101] peaks. Such kind of phase structure has been reported by other authors [8] for the thermal annealed CdS films obtained by chemical bath deposition (CBD). In spite of this, in Fig. 4 (lower) one can see that in the CSS CdS film the [100] and [101] peaks are not present, but, as the inset shows, there is a well marked [103] hexagonal reflection. Such diffraction pattern structure can be interpreted as a mixture of hexagonal and cubic (hawleyite) phase [10].

Figure 5 shows the as registered GIXRD diffraction patterns under 3°C of X-ray incidence, of the ITO/CdS/CdTe films. In Fig. 5 (upper), neither the CdS peaks nor the ITO peaks are present. This have to be related to the relatively high thickness of this film (~ 5.000 counts/s in the peak [111]), whereas in Fig. 5 (lower), the ITO and CdS peaks are perfectly defined. It evidences that this layer is very thin (~ 5.000 counts/s in the peak [111]). This behavior indicates that the PLD system can finely control the thickness of the films and is able to deposit thick as well as thin films. It is also interesting to indicate that the CdS film conserves its hexagonal crystalline structure with the complementary peaks in the [100] and [101] directions.

Figure 6 shows the results of the Auger analysis in the derivative mode of CdS (upper curve) and CdTe (lower curve) targets after 1 min of erosion with Ar^+ ions. Upper curve of Fig. 6 present low noise and well-defined peaks, related to the Auger S (LMM) and Cd (MNN) transitions with their minima at about 150 and 374 eV, respectively. An Auger spectrum of CdTe is present in the lower curve of Fig. 6, were the peaks related to Cd (MNN) and Te (MNN) transition appears at 375 and 483 eV, respectively. Figure 7 shows the Auger depth profile of the Glass/ITO/CdS/CdTe structure grown by PLD. In this Figure the different layers from the structure are shown. The peak to peak intensities of S, Cd and Te in the depth profile of the structure and CdS and CdTe targets are similar.

4. Conclusions

Simple, small and effective mechanism for multitarget and multisubstrate manipulation was designed and constructed. Using these mechanisms a multitarget system for growth of

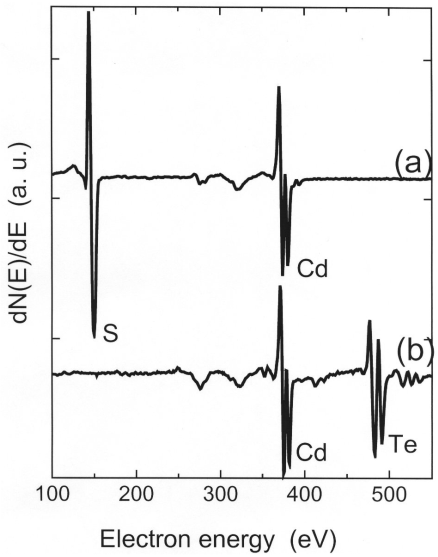

FIGURE 6. AES spectra of CdS (upper curve) and CdTe (lower curve) targets.

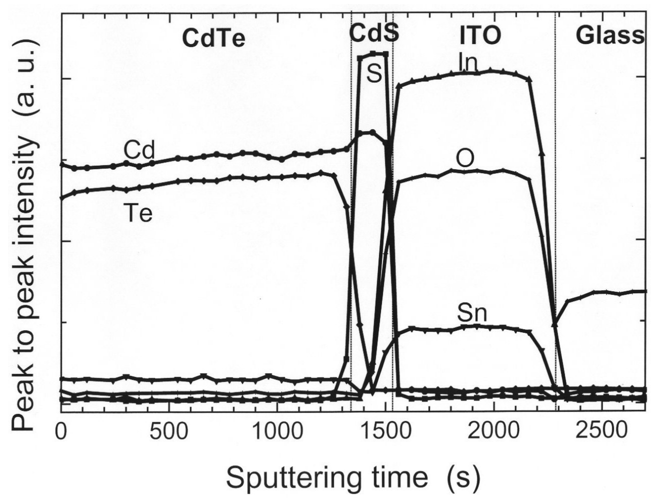

FIGURE 7. Depth profile obtained for the Glass/ITO/CdS/CdTe structure grown by PLD.

thin films by pulsed laser deposition was made. This system has proved to be very useful for the study of multilayer structures and the investigation of new materials. The ability of the system was evaluated by means of growing of ITO/CdS, ITO/CdTe, and ITO/CdS/CdTe structures. The grazing incidence X-ray diffraction study has demonstrated that our PLD multitarget system is able to grow good crystalline quality of thick or thin CdS and CdTe films on Glass/ITO substrates.

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