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CdTe:Sn thin films deposited by the simultaneous laser ablation of CdTe and Sn targets

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Abstract

CdTe:Sn thin films were grown by pulsed laser deposition on glass substrates at room temperature. The study of the changes in the chemical, structural and optical properties of the films as a function of the density of Sn ions calculated from Langmuir planar probe measurements is presented. Four films were grown by the simultaneous ablation of CdTe and Sn targets in vacuum. The Sn ion density was modified by varying the fluence on the Sn target, while the CdTe plasma density was kept constant for all the deposits. One CdTe film was grown as control sample using the same experimental conditions as in the CdTe:Sn films. The chemical composition was analyzed by XPS, where a dependence of the Sn incorporation into the CdTe lattice, on the Sn ion plasma density was demonstrated. The crystalline structure analysis by XRD showed a hexagonal structure for all the films. When the CdTe and Sn plasmas were combined, a preferential orientation in the plane (110) was observed for the resulting films. Furthermore, as Sn plasma density increased, the intensity of the (110) peak increased as well, suggesting that crystalline re-orientation is an effect of Sn incorporated into the CdTe lattice. Vibrational behavior was analyzed by Raman spectroscopy. A vibrational mode appeared at 118 cm⁻¹ and was related to a Sn–Te vibration, suggesting the incorporation of substitutional Sn into the CdTe lattice. The Sn–Te bonding was confirmed by XPS by the appearance of signals centered at 485 and 494 eV, which correspond to Sn²⁺ in SnTe. Thin films thicknesses values were between 320 and 460 nm increasing with Sn ion density. The band gap calculated using UV–vis spectrophotometry, resulted in values ranging from 1.42 to 1.46 eV. PL measurements showed a slight blue shift of the near-edge emission as Sn plasma density increased.

1. Introduction

Cadmium telluride (CdTe) films are suitable for application in optoelectronic devices such as solar cells and x-ray detectors due to its excellent optical and electrical properties [1–5]. One of the main characteristics of CdTe is that a layer of a few micrometers of thickness can absorb 90% of incident photons, because it has an optical bandgap of 1.5 eV and high absorption coefficient (>5 × 10⁵ cm⁻¹) [6]. CdTe can have both n or p-type conductivity, depending on impurity atoms such as Ge, Pb and Sn [7, 8]. Besides, CdTe presents interesting magnetic and optical properties [9–11]. In addition, it is well known that CdTe solar cells could reach maximum solar conversion efficiency values near to 34%. For those reasons, the interest in producing high quality layers of CdTe has increased in recent years. These films have been grown using deposition techniques such as atomic layer epitaxy [12], molecular beam epitaxy (MBE) [11], sputtering [5, 13], closed space sublimation [14, 15] and...
pulsed laser deposition (PLD) [1, 6, 16]. The PLD technique can produce high quality layers of many different materials, with the possibility of obtaining stoichiometric films with excellent physical properties. It has been demonstrated that the diagnosis of the plasma produced by the laser ablation of the target, allows a precise control of the structural properties even at room substrate temperature for different materials [16, 17]. When the plasma parameters (mean kinetic ion energy and density) are measured and thus, monitored, highly reproducible experiments can be performed and the properties of the growing films can be precisely controlled; in addition, the combination of two laser produced plasmas, offers the possibility of synthesize alloys, compounds, composites or doped materials [18–20]. In particular, control in doping processes of semiconductors can become complex in PLD because multiple targets with specific compositions should be synthesized in order to vary the content of a doping element in a film. The plasma parameters control of the combination of plasmas produced from a semiconductor material and a doping element, can result in a very efficient tool to study the incorporation of impurities in semiconductor lattices.

In this work, we report the effect of the combination of CdTe and Sn plasmas by the simultaneous ablation of Sn and CdTe targets on the chemical, structural, morphological and optical properties of CdTe:Sn films when the Sn plasma density was varied while CdTe plasma parameters were kept constant. Results are discussed as a function of increasing Sn plasma density.

2. Experimental details

CdTe:Sn thin films were grown on corning glass substrates by PLD. A 1 inch CdTe target obtained compressing high purity CdTe powders (99.99% from Sigma-Aldrich), was placed perpendicular to a 1 inch Sn target obtained by melting Sn pellets (99.99% from Kurt J Lesker) in argon atmosphere to avoid oxidation. Separation between the center of the CdTe target and the surface of the Sn target was kept constant at 5.5 cm. The targets were simultaneously ablated in order to produce a combined plasma. Figure 1 depicts a schematic diagram of the PLD system. The CdTe target is located in front of the substrate at a distance of 5 cm. The Sn target is perpendicular to the CdTe target separated a distance of 3.7 cm as measured from the Sn surface to the ablation spot in CdTe. The ablation spot of the Sn target is separated by 6.2 cm from the substrate. For the ablation process a Nd:YAG laser with 600 mJ of maximum output energy, at a wavelength of 1064 nm, 6 ns pulse width, and repetition rate of 10 Hz was used. The beam was divided into two equal beams using a beam splitter. One beam was focused on each target while they were rotating at 15 rpm to avoid drilling. Depositions were carried out in vacuum at a pressure of $6 \times 10^{-5}$ Torr and 10 min of ablation time.

The individual laser produced plasmas were analyzed by Langmuir probe characterization prior to each deposition. A 6 mm diameter planar Langmuir probe biased at $-48$ V was used for plasma measurements. The probe current was obtained by measuring the voltage drop across a 20 $\Omega$ resistor using a Tektronix 500 MHz...
digital oscilloscope. The planar probe replaced the substrate in order to set the plasma parameters before each deposition. The plasma parameters such as mean kinetic ion energy and plasma density were estimated by the time of flight curves (TOF) using the procedure described in references [21, 22] respectively. A reference TOF curve was set for the CdTe plasma; in order to have the same CdTe plasma conditions, the TOF curve for CdTe was reproduced for all the experiments. Sn plasma parameters were varied by the modification of the incident energy on the Sn target. Four films were deposited by combining the plasmas with the aim of changing the Sn content incorporated into the CdTe lattice and they were compared with the CdTe reference sample.

Sn content in the films and Sn oxidation state were determined by x-ray photoelectron spectroscopy (XPS), using a monochromatic Al Kα x-ray source and a hemispherical energy analyzer PHOIBOS 100. High-resolution spectra were collected with steps and pass energy of 0.1 and 20 eV respectively. The depth profiling was applied by rastered Ar⁺ ion sputter etching over an area of 4 × 4 mm² with a voltage acceleration of 5 kV and multiple periods of five minutes until reaching the substrate. The structural analysis was performed by x-ray diffraction (XRD) and Raman spectroscopy. XRD patterns were acquired in a PANalytical Empyrean diffractometer, Raman measurements were carried out in a Horiba Jobin Yvon HR 800 Raman spectrometer with the 532 nm excitation line, the beam was focused using a 50x objective lens. Thickness of the films was measured by profilometry with a KLA Tencor D-120 profilometer. Surface morphology was observed by scanning electron microscopy (SEM) with a Tescan Mira 3 with secondary electrons using 20 kV as accelerating voltage.

Optical characterization was carried on by means of UV–vis and room temperature (RT) photoluminescence (PL) spectroscopies measurements, obtained using a Genesys 10uv, Thermo UV–vis spectrophotometer, and a Horiba spectrofluorometer model fluoromax-4, respectively.

3. Results and discussion

Figure 2 shows the TOF curves for the Sn plasmas. The inset of figure 2 corresponds to the TOF curve for the CdTe plasma, which was reproduced for all experiments to ensure having the same CdTe plasma conditions in all the deposits. It can be noticed that the calculated ion density for Sn increases as the height of the curves increases, the expression used for density calculation, described in reference [22] is 

\[ N_p = \frac{I_{\text{max}}}{e \nu A} \]

where \( e \) is the electron charge, \( \nu \) is the plasma flow velocity and \( A \) is the collecting area of the probe. \( I_{\text{max}} \) corresponds to the maximum current value of the curve (saturation current). The Sn ion density was changed from \( 8 \times 10^{11} \) to \( 19 \times 10^{11} \) cm⁻³, while the plasma density for CdTe was \( 2 \times 10^{14} \) cm⁻³. It can be expected that variation in plasma density values would change the Sn amount incorporated into the CdTe lattice and thus, the physical properties of the films. Notice that there is difference between ion density for CdTe and Sn of approximately 3 orders of magnitude. This difference was chosen looking to produce doping and to avoid segregation or formation of Sn and/or Sn compounds.

In order to analyze the effects of increasing Sn ion density on the incorporation of Sn into the CdTe films, XPS measurements were performed. According to the results shown in figure 3, where a graph of elemental atomic percentages of Cd, Te and Sn (left y-axis) and Cd/Te ratio (right y-axis) versus Sn ion density is presented, it can be clearly seen that atomic composition is affected by increasing Sn ion density. The Cd/Te
ratio was calculated from XPS measurements by considering the binding energy signals for Cd 3d5/2 and Te 3d5/2. The CdTe film grew with a Te excess, this effect has been observed before for films grown at similar plasma conditions [16]. However, when the CdTe and Sn plasmas are combined, the Cd/Te ratio was modified; values above 8 × 10¹¹ cm⁻³, yield films with Cd excess. Regarding Sn atomic content, it can be observed that Sn was incorporated into the CdTe films at levels below 1 at%, and there is a relation between Sn ion density and Sn atomic content in the samples, increasing from 0.1 to 0.5 at% as density rises. The importance of having the possibility of changing the Cd/Te ratio lies in that electrical properties are dependent on the composition, i.e. Te excess films produce p-type conductivity [6], while Cd excess yields n-type conductivity [6]. On the other hand, optical properties, such as absorption coefficient or band gap can be modified by doping with different elements.

It is important to mention that due to the targets configuration, it could be expected that composition and thickness inhomogeneity exist in the samples; however, the deposited area consists in circles of 1 cm diameter, thus, at least for this area we can consider the films to be quasi-uniform both in composition and thickness.

In order to inspect whether the incorporation of Sn into CdTe was substitutional or interstitial, XRD patterns were analyzed. Figure 4 shows the diffractograms of the CdTe along with the CdTe:Sn samples. It can be observed that the CdTe film has a hexagonal structure, which agrees with previous reports [16, 20]. Regarding the CdTe:Sn patterns, notice that the hexagonal structure is conserved, however, the films are oriented in the (110) direction. Although this orientation is not usual for CdTe, similar results have been reported when doping CdTe with Cu by combining Cu and CdTe pulsed laser produced plasmas[20].

Figure 3. Atomic content of Sn (left axis) and Cd/Te ratio (right axis) as a function of Sn ion density.

Figure 4. X ray diffraction patterns for the samples.
It is known that substitutional incorporation of some metals at doping levels, can enhance the crystallinity of the hosting matrix, thus, the (110) orientation could be related to the presence of substitutional Sn in the CdTe matrix. However, the interaction of plasmas plays an important role for the obtained orientation as it has been observed for CdTe:Cu grown by PLD [20].

Surface morphology of the films can be observed in the SEM images presented in figure 5. As it has been observed before for PLD grown CdTe [16], the surface is very smooth with the presence of some droplets. Increasing Sn ion density does not have considerable effects on the surface morphology, however, in sample CdTe:Sn14, the presence of several fragments can be noticed. This effect could be caused by film delamination due to the existence of zones with poor adherence of the films to the substrate.

Figure 5. Scanning electron micrographs of CdTe and CdTe:Sn samples.
Raman spectroscopy characterization was carried out to observe changes on the vibrational modes as Sn ion density increases. The Raman spectra of the samples are shown in figure 6. The spectrum of de CdTe sample shows 3 vibrational modes centered at 120, 140 and 163 cm\(^{-1}\) corresponding to the \(A_1(\text{Te})\), \(E_1(\text{Te}) + \text{TO (CdTe)}\) and \(\text{LO (CdTe)}\) vibrational modes \([16]\). For the Sn doped samples, similar Raman spectra can be observed, nevertheless, the band centered at 120 cm\(^{-1}\) shifts to 118 cm\(^{-1}\). This signal has been assigned to the \(A_1\) vibrational mode of Sn-Te \([23]\). The appearance of the Sn-Te vibrational mode as Sn ion density increases indicates that there exist Sn atoms substituting Cd in the CdTe lattice, which is in agreement with XRD results.

In order to further confirm the substitutional incorporation of Sn in the CdTe lattice, high resolution XPS spectra were recorded. Figure 7 shows the high resolution XPS spectra for the Sn containing samples for a binding energy range of 480–504 eV. Weak signals centered near 485 and 494 eV can be observed for all the Sn doped samples. Notice that as Sn ion density increases, the intensity of the XPS signals also increases. Saghir \textit{et al} \([24]\) reported that a binding energy of 485.4 eV corresponds to Sn\(^{2+}\) in SnTe, thus, for the present results it can be concluded that Sn\(^{2+}\) are present in the films, which means that Sn substitutes Cd as both have the same oxidation state.

The effect of Sn doping of CdTe on the optoelectronic properties was studied by UV–vis and PL spectroscopies. The bandgap (\(E_g\)) of the samples was estimated from UV–vis absorbance (optical density, O D)
measurements. For the calculation the Tauc relation was used \cite{1} by extrapolating the linear part of the \((O\ D \ h\nu)^2 \) versus \(h\nu\) plots to the x axis, where \(h\nu\) is the photon energy. Tauc plots are shown in figure 8.

As it can be observed in figure 8 the optical bandgap for CdTe is 1.43 eV, which agrees with the reports in literature \cite{3, 15}. Incorporation of Sn induces a slight band gap increase, although no clear trends for increasing Sn ion density can be observed. Nevertheless, it can be considered that increasing Sn ion density does not have a considerable effect on the band gap for the films.

In order to have a better understanding of the optical behavior of the films as the Sn ion density increases, PL spectroscopy measurements were performed. Figure 9 shows the PL spectra of the films. As it can be observed, the CdTe sample exhibits a band centered at 1.5 eV, which agrees with an emission corresponding to a near edge transition for CdTe \cite{16}. As Sn ion density increases, the near edge emission slightly shifts to higher energies, which is in agreement with UV–vis measurements. This shift is an effect of the incorporation of Sn into the CdTe lattice, which modifies the crystalline orientation, and thus the electronic band structure of CdTe.
4. Conclusions

Substitutional incorporation of Sn into a CdTe matrix was successfully achieved by the combination of Sn and CdTe plasmas in a PLD process. The Sn content in the films was varied from 0.1 to 0.5 at% due to the Sn plasma density variation which can be controlled by means of Langmuir planar probe measurements. The appearance of a Raman vibrational mode centered at 118 cm$^{-1}$ was related to the substitutional incorporation of Sn into the CdTe lattice and associated to the A$_1$ Sn-Te vibration. The calculated band gap for the CdTe and CdTe:Sn films was around 1.43 eV. A preferential orientation on the (110) direction was induced by the incorporation of Sn into the hexagonal CdTe structure.

It was demonstrated that plasma diagnosis is a powerful tool to monitor and control dopants on CdTe lattices.

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