PbTe thin films grown by femtosecond pulsed laser deposition.

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Abstract
PbTe thin films were grown on BK7 glass and Si(100) substrates using femtosecond pulsed laser deposition at room temperature. The influence of the background pressure and the laser fluence on the structural and optical characteristics of the PbTe films was studied. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used to characterize the surface and structural properties of the deposited PbTe thin films, respectively. Transmission spectroscopy measurements in the visible and infrared region (VIS-IR) were used to investigate the optical properties of the PbTe thin films.

1. Introduction
Lead telluride (PbTe) is an important group IV-VI semiconductor with a narrow fundamental band gap $E_0 \approx 0.3$ eV at room temperature. Extensive research has been done in the last two decades on PbTe thin films, mainly due to the technological importance for use in a variety of optoelectronic devices like infrared detectors and tunable mid-infrared quantum well diode lasers[1]. PbTe thin films have been deposited using techniques such as hot-wall epitaxy[2], magnetron sputtering[3], thermal evaporation[4], electrodeposition[5], molecular beam epitaxy[6] and pulsed laser deposition[7,8,9]

More recently, PbTe grown in form of Quantum Dots is been studied because of its interesting non linear optical properties. The fact that PbTe present quantum conminements effects in the region used for optical communications [10,11] transforms this material in an excellent candidate for developing all-optical switching devices.

Pulsed laser deposition (PLD) is a thin film growth method which has generated a lot of interest in the past few years as one of the simplest and most versatile technique for the deposition of a wide variety of materials. PLD enables easy stoichiometric transfer from the target to the deposit in a convenient gas atmosphere, becoming a powerful technique for fabricating high-quality films of high-Tc superconductor oxides and a number of others, such as piezoelectrics and ferroelectrics. More recently, this technique was used to deposit polycrystalline and epitaxially oriented films of PbTe on KCl(100) and BaF2(111) substrates [12,13].

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The major disadvantage of PLD has been the deposition of particulates or droplets (splashing) on the film surface during the deposition process. The splashing formation is a great drawback for applications related to the fabrication of nanostructured materials. Obviously, the arrival of micron or submicron sized particulates at the substrate is detrimental to the properties of an optical device based on nanoparticles.

With the rapid development experienced in the generation of ultra short laser pulses, new possibilities were opened for the PLD technique by using femtosecond lasers as ablation source. It is commonly believed that when the temporal length of the laser pulse became shorter than the several picoseconds required to couple the electronic energy to the lattice of the material, thermal effects could not play a significant role. Since the pulsewidth is too short for thermal effects to take place, the material is direct vaporized away from the surface.

Nevertheless, more recently other processes have been suggested to occur during the interaction of material with ultra-short laser pulses. Rousse et al [14] suggested the ultra-fast melting of semiconductors which is believed to arise from the modification of the inter-atomic forces and can occur to much shorter times than the time needed for thermal effects.

So far most of the research on PLD for the fabrication of PbTe thin films has concentrated on the use of high energy solid-state Nd:YAG or excimer lasers whose output energy is typically hundreds of mJ in 5-10 ns duration pulses at a repetition rate of 10-100 Hz. There is little in the current literature on PbTe thin films grown by femtosecond PLD. In this sense, the aim of this work is to investigate the influence of the principal growth parameters on the properties of PbTe thin films grown by femtosecond PLD.

2. Experimental

Experiments were carried out using a typical PLD configuration comprising a deposition chamber and an ultra short pulsed laser.

The deposition was performed in a stainless steel vacuum chamber pumped to a base pressure of 10^-7 mbar. PbTe thin films were grown at room temperature in high purity argon atmosphere. The details of the deposition system have been described previously elsewhere [15,16].

A short pulse of low energy from a pulsed Ti:sapphire laser (Coherent Mira 900, 100 fs, average power ~ 500 mW, repetition rate 76 MHz) was used as the seed pulse. The pump pulse was provided by a Nd:YAG laser (8ns, 400 mJ). Both seed and pump pulses were fed into a regenerative amplifier yielding ultra-short pulses of high energy (100 fs; 30 mJ) at a central wavelength of 800 nm (photon energy of 1.55 eV). The output beam diameter was 8 mm. The laser was operated in continuous shot mode with a pulse frequency of 10 Hz. The femtosecond laser beam was focused with a lens (f=30 cm) at approximately 45° onto a rotating PbTe target.

In order to investigate the effect of the background pressure on the structural and optical characteristics of the PbTe thin film the pressure was varied from 10^-1-10^-3 mbar. Moreover films were grown at laser fluences from 0.12-3.8 J/cm^2 (1.2 – 38 TW/cm^2) to study the influence of this parameter in the film properties.
The structural analysis of the samples were obtained by means of X-ray diffraction at room temperature (T ≈ 300K) using θ:2θ scans in Philips (PW 11700) diffractometer system with Kα radiation (λ=1.93597Å) and a graphite monochromator for diffracted beam. The measurements were obtained using 0.02° step size and 2s/step.

The surface morphologies of the PbTe thin films were studied using a Jeol scanning electron microscope (FEG JSM 6330F). Ultraviolet-NIR optical transmissions spectra of the PbTe thin films were recorded using a Perkin Elmer (Lamda 9) spectrophotometer.

3. Results and discussion

It is a common procedure in PLD when a new material is ablated or a new evaporation source is used to begin by growing thin films in order to study the influence of the growth parameters in the properties of the films. In the present work, experiments were conducted both at different background pressures and laser fluences to determine the influence of these important growth parameters in the properties of the PbTe films.

3.1 Surface morphology of the PbTe thin films growth at different laser fluences.

Laser fluence can be changed by varying both the laser energy and the laser spot diameter. Initially films were grown at 0.2 mbar argon and different laser energies: 30mJ/pulse and 5 mJ/pulse. Under these conditions the laser fluence at the target side was 3.8 J/cm² (38 TW/cm²) and 0.6J/cm² (6 TW/cm²), respectively. SEM images of films grown at these conditions are shown in figure 1.

The film surface shows a great number of small-sized particulates (nanometer range) and a few larger particulates micron or sub-micron sized. Both the small and the larger particles are most probably fused material ejected from the target during the femtosecond laser irradiation. No significant differences are observed between films grown at lower or higher laser fluences in the studied range.

![Figure 1: SEM images PbTe films grown by PLD using ultra short pulses and laser fluence of (a) 3.8 J/cm²[38 TW/cm²] and (b) 0.15 J/cm²[1.5 TW/cm²]. Samples were fabricated at 0.2 mbar argon, with 100fs laser pulses, λ=800 nm and repetition rate 10 Hz.](image-url)
PbTe thin films were also grown at a lower fluence by increasing the laser spot diameter. Using the highest available laser energy (30 mJ/pulse) and increasing the spot diameter the laser fluence at the target side was calculated as 0.15 J/cm² [1.5 TW/cm²]. PbTe thin films fabricated under these conditions are presented in figure 2.

![Figure 2: SEM images of PbTe films grown by PLD using ultra short pulses (100 fs) and laser fluence of 0.15 J/cm² [1.5 TW/cm²] and different number of laser pulses: (a) 1200 laser pulses; (b) 300 laser pulses. Samples were fabricated in 0.2 mbar argon atmosphere.]

The sample surface for both samples exhibits similar features. Due to the spot size increase, the deposition rate considerably increased enabling the fabrication of a thin film with a few laser pulses. To eye vision the films are very rough exhibiting a poor adherence to the glass substrate. SEM images of the film surface showed a huge number of particulates ranging from nanometer to micron size.

Despite the times involved in the laser-target interaction are shorter than the times required to thermal effects occur, the formation of a liquid film on the sample surface after irradiation with ultra-short laser pulses was the most probable mechanism proposed by Rousse et al [14]. The ultra fast melting mechanism could explain the surface morphology of the films fabricated in the present work.

The wavelength used for the evaporation can also contribute to the presence of particulates in the film surface. 800 nm is not totally absorbed at the target surface; it can penetrate in the target producing splashing.

3.2 Analysis of the target surface after irradiation with ultra-short laser pulses.

The supposition of a liquid film layer formation at the target surface was reinforced by studying the target surface after irradiation with 10 laser pulses (100 fs) and different laser fluences as shown in figure 3. SEM images reveal similar features for all
the laser fluences studied. (a) there are visible fractures contraction joints on the target surface indicating the interaction with a huge shock wave, (b) nanometer sized, submicron and micron-sized particulates are also visible on the target surface similar to those found on the film surface, (c) laser induces surface structures are also visible in some regions of the spot, the depth of which increases by increasing the laser fluence.

Figure 3. Target surface after irradiation with 10 ultra-short laser pulses (100 fs) and (a) 5mJ(0.6J/cm²), (b) 10mJ(1.27J/cm²); (c) 20 mJ(2.5J/cm²) and (d) 30 mJ(3.8J/cm²)

3.3 Influence of the background pressure in the PbTe thin films properties.

To study the influence of the background pressure in the film properties, PbTe thin films were fabricated at different background pressures ranging from 2 x 10⁻¹ mbar to 2 x 10⁻³ mbar argon and keeping constant all other growth parameters. Results obtained for these studies are shown in figure 4. No significant differences were observed at the film surface for the samples grown in the studied pressure interval. The film surface for all samples
shows a great number of small-sized particulates (nanometer range) and a few larger particulates micron or sub-micron sized.

Figure 4: SEM images of PbTe thin film grown by PLD at different background pressures in the vacuum chamber: (a) $2 \times 10^{-1}$ mbar; (b) $2 \times 10^{-3}$ mbar. The samples were fabricated with the following parameters: laser fluence 0.6 J/cm$^2$ ($6 \text{TW/cm}^2$), $\lambda=800$ nm and repetition rate: 10 Hz.

3.4 Crystalline quality of the PbTe thin films

XRD results for PbTe films grown at different pressures and laser fluences are presented in figure 5. The results show that the thin films grow basically in the face centered cubic (fcc) PbTe structure. Samples grown at different fluences by changing the laser energy and having a tighten laser spot (Sa01 and Sa09) exhibit a certain degree of crystallinity with a well defined (200) peak. Both samples show similar XRD pattern despite they were grown at different background pressures. The film surface of samples Sa01 and Sa09 were presented in figure 1(a) and figure 4(b), respectively.

Samples grown at lower fluences, by increasing the spot size at the target (Sa03) show seven peaks in the diffraction pattern also associated to the PbTe fcc structure. Crystallographic direction and d-spacing among other relevant data of these peaks are presented in table I. The presence of a lot of peaks revealed the poor crystallinity of these samples whose surface was presented in figure 2.
Table I: Principal data of the peaks observed in the XRD patterns which are related to PbTe fcc. The films were fabricated by PLD technique using ultra-short laser pulses as ablation source.

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Figure 5: XRD pattern of PbTe thin films grown at different pressures and laser fluences. Samples Sa01 and Sa09 were fabricated at different background pressures and different laser fluences. Laser fluence for Sa01 was higher by increasing the laser energy and keeping constant the spot size. On the other hand, samples Sa01 and Sa03 were fabricated at the same background pressure and with different laser fluences. Laser fluence of Sa03 was lowered by keeping constant the laser energy and increasing the spot size. For comparison the XRD pattern of the target was also included.

3.5 Absorption measurements.

Absorption measurements were conducted using a Perkin Elmer Lamda 9 spectrometer in the region from 200 to 2500 nm. Absorption spectra (figure 6) show
peaks near 600 nm (2.08 eV) and 1000 nm (1.21 eV) which agree with energy levels present in the PbTe band structure reported by Suzuki et al. \cite{17}

Figure 6: Absorption spectra of PbTe thin films grown by PLD technique using ultra-short laser pulses. For comparison the absorption spectrum of the BK7 glass substrate is also presented.

4 Conclusions
The study reported in this work was conducted to investigate the influence of basic growth parameters on the structural and optical characteristics of PbTe thin films deposited on Si(100) or BK7 glass substrates using femtosecond PLD. At the studied laser fluences there is no significant influence of the pressure on the density of particulates on the film surface. A diminution in the laser fluence by increasing the spot size resulted in PbTe thin film with poor crystallinity.

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References


