Pulsed laser ablation and deposition of ZnS:Cr

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We present a method to deposit films with a range of doping concentrations/dilute alloys, from a single target in pulsed laser deposition (PLD). Cr-doped ZnS films were deposited by ablating a target consisting Cr particles (diameter 20–100 μm) embedded in a ZnS:Cr matrix. The Cr content in the film was varied in the range 2.0–5.0 at.% simply by varying the laser fluence, or by varying the number of pre-ablation pulses. Such a doping/composition range is normally not achieved using a single target in PLD. Details of the target ablation study, which is needed prior to the deposition, are also presented.

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1. Introduction

Cr-doped ZnS (ZnS:Cr) is an interesting material that potentially can be used for various spintronic [1,2] and optoelectronic applications [3]. In particular, ZnS:Cr is proposed as an intermediate band (IB) material by ab initio calculations [4] for use in intermediate band solar cells (IBSCs) [5].

Doped ZnS thin films have been deposited using several methods [6], and PLD is regarded as a very promising technique [7], although depositing films with varying doping concentrations can be challenging: the conventional method is to ablate a single target for each composition, since stoichiometric transfer occurs in most cases in PLD [8], although non-stoichiometric transfer also can occur [9]. A drawback of this technique is that the dopant concentration is fixed and varying it requires production of several targets, which is a time consuming task. Mn doping [10] and Co doping of ZnS [11] and Zn0.9Cd0.1S [12] have been achieved using this conventional method. Another method to deposit doped films by PLD is to ablate two or more target materials simultaneously by a dual beam system [13] or sequentially by changing the target before a full monolayer forms [14]. Sequential ablation of several targets can also be done by scanning the laser beam on fixed targets. These methods require specially designed chambers and computer controlled PLD systems. Therefore, it would be advantageous if various doping concentrations can be obtained from a single target simply by varying the growth parameters.

In this article, we therefore present a method to vary the doping content of pulsed laser deposited thin films using a single target consisting of Cr particles (20–100 μm) embedded in a ZnS:Cr matrix. Using such a binary target, the film stoichiometry could be controlled by varying the laser parameters such as laser energy density (fluence) and/or the number of pre-ablation pulses prior to deposition. A similar method has been used for CuZnS, where the Cu content varied with laser fluence [15], but in that work no information about ablation and deposition processes are given.

2. Experiments

For ablation and deposition of Cr-doped ZnS, a commercial target (ZnSCr) was purchased from Super Conductor Materials, Inc. According to the information received with the target, the purity was 99.99% and the chemical formula was (ZnS)0.94Cr0.06. Therefore, the Cr content in the target was 6/194 or about 3 at%. However, the Cr content was not uniformly distributed in the target. Indeed, the target was consisted of Cr particles (20–100 μm) embedded in a matrix containing very low amount of Cr, and it was not trivial to be determined, especially due to the presence of Cr particles with close distances from each other. The density of the ZnSCr target was determined and was 70%. We also used a Cr chip (99.999% pure) and two polycrystalline (undoped) ZnS targets, one with 90% density (99.99% pure, Kurt J. Lesker) and the other with 60% density (99.99%, Super Conductor Materials, Inc.) for additional ablation studies. A KrF excimer laser (Lambda Physics COMPex Pro 110, 248 nm, 20 ns) was operated at 5 Hz to ablate the targets (at 45°). The center part of the laser beam was imaged onto the target, to obtain a uniform fluence within the laser spot on the target. The laser spot size, Ao, on the target was ~1 × 2 mm², unless otherwise specified. The laser fluence, φ, was varied between 1.0–7.8 J/cm². To determine the change in thickness of the target per pulse (the material removal rate per pulse), Δh, ablation at a fixed location was performed.

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Fixed spot' refers to ablation in a fixed location on the target, i.e., without scanning the target. The spot was ablated by \( N_p = 400 \) or \( N_p = 1000 \) pulses and \( \Delta h \) was obtained by dividing the total depth of the spot divided by \( N_p \). The chamber base pressure was \( = 5 \times 10^{-6} \text{ Pa} \), and a background pressure of 0.3 Pa Ar, gas flow 22 SCCM, was used during both ablation studies and film growth. Cr-doped ZnS films were deposited at 550 °C on Si[100] substrates. Prior to film growth, the substrates were degreased using ethanol and acetone, and they were etched in 5% HF for 3 min followed by 3 min rinsing in deionized water in order to remove the native oxides on Si. Next, the substrates were transferred to the growth chambers, and heated (at base pressure) to 850 °C. The substrates were kept at high temperature for 2 min and then the temperature was lowered to the temperature used during growth. The target was scanned during deposition, so a rectangular area of \( 10 \times 20 \text{ mm}^2 \) was ablated. 15,000 pulses was used for deposition of the film. The target to substrate distance was 7 cm.

Before each deposition the target was polished and pre-ablated by certain number of pulses, \( N_p \). Polishing was performed using different SiC sandpapers ranging from course to very fine grit sizes in several steps, that is P600 (ISO/FEPA grit designation), P1210, P2500, P4000, P8000, and P12000 as the last step. To keep the polishing process as simple as possible and to avoid any contamination of the target, no solvent was used during the polishing. As measured by profilometer, RMS roughness of nearly 250 nm was achieved after polishing the target surface.

The ZnSCr target surface was studied by scanning electron microscopy (SEM) before and after ablation. The structure and composition of the polished targets were studied by X-ray diffraction (XRD) using Cu radiation (Bruker D8 Focus) and energy dispersive X-ray spectroscopy (EDS) respectively. The Cr distribution in the ablated target was also obtained by EDS. Material removal from the targets was measured by profilometer (Dektak 150). Profilometer was also used for film thickness and growth rate measurement of the films. XRD was used to study film structure, and Rutherford backscattering spectroscopy (RBS) was utilized to determine film composition. RBS measurements were made with 1.6 MeV He ions backscattered into the detector at 165° relative to the incident beam direction. The film compositions were determined by fitting simulated curves to the experimental spectra using the SIMNRA code [16].

3. Results and discussions

The XRD pattern of the ZnSCr target before ablation is shown in Fig. 1(a). We can see a Cr related XRD peak at \( \theta = 44.4° \). All other peaks are related to the matrix. Both zincblende (Z) and wurtzite (W) phases of ZnS are present in the matrix. Note that some of the XRD peaks in zincblende phase overlaps with peaks in wurtzite phase, so the actual phase of the target cannot be determined by \( \theta - 2\theta \) XRD scans. A SEM image of the polished target is shown in Fig. 2(a), and we see that the target is not uniform. EDS data (not shown) identified the darker areas as Cr with no Zn content. The matrix consisted of ZnS:Cr, but the Cr content in the matrix was not determined. The areas with metallic Cr also appeared specular by visual inspection. The laser ablation modified the surface and pillars oriented toward the laser beam were formed. The surface ablated using \( \phi = 4.6 \text{ J/cm}^2 \) for \( \sim 300 \) pulses in a fixed spot, is shown in Fig. 2(b). An EDS map of Cr (red areas) in the same figure clearly shows that Cr is found mainly on top of the pillars, but there is also some Cr in the matrix.

To analyze the ablation of the ZnSCr target, we first focus on the fixed spot ablation. An example of a fixed spot ablated by 160 pulses at \( \phi = 2.3 \text{ J/cm}^2 \) is shown in Fig. 2(c). The SEM images in Fig. 2(d)–(i) show the ablated surface of the target by 20, 80 and 160 pulses, for \( \phi = 2.3 \text{ J/cm}^2 \) and \( \phi = 4.6 \text{ J/cm}^2 \). From the SEM images we observe that with increasing number of laser pulses, the length of the pillars increases. Fig. 3 presents the density of pillars formed by single spot ablation. At a given fluence, higher number of laser pulses per spot resulted in higher density of pillars. At a given number of pulses, an increase in the density of pillars was observed when fluence was increased from 2.3 to 4.6 J/cm² (between 6% to 20% depending on the number of pulses).

The ablated surface between the pillars on the ZnSCr target is shown in Fig. 4(a). The holes in the ablated surface are probably caused by the low target density, see also Fig. 2(a). In addition, the surface appears melted, and the same is seen for the Cr chip in Fig. 4(b). \( \Delta h \) for the Cr chip, the ZnSCr and the two ZnS targets are shown in Fig. 4(c). We see that there is almost no ablation of the Cr chip for \( \phi = 4 \text{ J/cm}^2 \), and \( \Delta h \) increases rapidly at \( \phi > 4 \text{ J/cm}^2 \). In contrast, the ZnS and ZnSCr targets are significantly ablated for all fluences used. \( \Delta h \) also depends on the target density: \( \Delta h \) increases when the target density decreases, see Fig. 4(c). Furthermore, with increasing laser fluence, \( \Delta h \) increases almost linearly for the ZnSCr and ZnS targets.

Next, we focus on the ablation of the ZnSCr target during target scanning, i.e., the situation during thin film deposition. The SEM images of the ZnSCr target ablated by 7000, 22,000, 37,000 and 200,000 pulses are shown in Fig. 5(a)–(d), respectively. These values are the number of pre-ablation pulses, \( N_p \), used for ablation of an area of \( \sim 2 \text{ cm}^2 \). Since the scanned area was 100 times larger than the laser spot size, the total number of pulses used for ablation of the whole area divided by 100 is an upper limit for the number of pulses per spot. As can be seen from the figure, the density and length of the pillars increases with increasing number of laser pulses. However, the surface in Fig. 5(b) and (c) are very similar. This indicates that after a large number of preablation pulses, e.g., \( N_p \geq 22,000 \), the rate of change of the morphology decreases. Therefore, a uniform film growth is expected when the number of pulses used during deposition is low enough, e.g. about 15,000 for the case studied here.

The material removal rate depends on optical and thermal properties of the target, as well as on the laser parameters. Despite the presence of Cr in the matrix, and possibly some Zn or S in the Cr particles, we compare the optical and thermal properties of ZnS and metallic Cr, given in Table 1. We see that for both materials the optical penetration depth, \( l_p \), is much smaller than the thermal diffusion length, \( l_T \). This means that the influence of direct bond breaking (photo-chemical ablation) on material removal is negligible, and thermal processes dominate material removal rate (photo-thermal ablation). We do not consider temperature dependence of the optical and thermal properties, more complex phenomena such as multi-photon or nonlinear optical absorption, nor the effect of defects and impurities on the absorption coefficient. However, with such a simplified picture we can still understand the ablation mechanism.

With thermally activated processes there is no threshold fluence, \( \phi_{th} \), for ablation to occur. However, above a certain fluence there is significant ablation (a few nm per pulse), and in accordance with Ref. [17], we define this fluence as \( \phi_{th} \). As we saw in Fig. 4(c), \( \phi_{th} \) is higher for

![Fig. 1. XRD pattern of the ZnSCr target before laser ablation (a), three ZnS:Cr films with Cr content of 2.0 at.% (b), 3.3 at.% (c), and 5.0 at.% (d), and Si substrate (e).](image-url)
Cr than for ZnS, as expected for two reasons: i) Cr has higher reflectance, so less photonic energy is coupled into it compared to ZnS, and ii) Cr has a higher thermal diffusivity, so the absorbed energy can diffuse into a larger volume of Cr in comparison to ZnS, within the same time frame. ϕ_{th} is typically 1–10 J/cm² for metals, while for inorganic insulators and strong-to-medium absorbers it is between 0.5–2.0 J/cm² (see p. 253 in Ref. [17]). In photothermal ablation using nanosecond pulses and ϕ ≤ ϕ_{th}, the overall material removal can be described by an Arrhenius-type law [17]

\[ Δh = C_1 \exp(-C_2/ϕ), \]

where C₁ and C₂ are constants, while with ϕ > ϕ_{th}, Δh can be described by a linear law

\[ Δh = B(ϕ - ϕ_{th}), \]

where B is a constant [17].

Accordingly, the formation of pillars on the ZnSCr target results from the lower ablation rate (smaller Δh) for the Cr particles compared to the surrounding ZnS-Cr matrix. The pillars consist of matrix material, with a Cr particle on top. The length of the pillars increases with increasing number of laser pulses. Eventually some of the pillars break and fall off. Once a pillar is broken, the exposed surface consists of the ZnS-Cr matrix material, not Cr. Broken pillars have a surface almost perpendicular to the laser beam, so they are rapidly ablated and vanish with continued laser ablation. In addition, varying ϕ has little effect on the density and length of the pillars since Δh for the matrix does not increase rapidly, but slowly and linearly, with increasing laser fluence, see Fig. 5(c). Note that the pillars are linked to the well-known cone-shaped features on pulsed laser ablated surfaces [21], that result from local changes in surface composition, morphology or crystalline structure. For instance, impurity-driven cone formation during laser sputtering of graphite has been reported previously in Ref. [22] where metal inclusions of 1 to 3 μm caused cones of about the same size.

![Fig. 2. SEM images of the ZnSCr target (a) before and (b) after (Cr in red) ablation, and (c) fixed spot ablation with ϕ = 2.3 J/cm² and 160 pulses. Fixed spot ablation 20–160 pulses and ϕ = 2.3 J/cm² (d)–(f), or ϕ = 4.6 J/cm² (g)–(i). (Color online.).](image1)

![Fig. 3. Density of pillars for single spot ablation of ZnSCr target.](image2)

![Fig. 4. SEM micrograph of the ablated ZnSCr target in the space between the pillars (a), and Cr chip (b) show direct evidence of photo-thermal ablation. Material removal rate per pulse, Δh, as a function of laser fluence, for ZnS with densities 60% and 90%, ZnSCr and Cr (c). N_s is the total number of pulses used for these fixed spot ablations.](image3)
We also studied selected properties of the deposited films. Additional results will be presented in another paper [23]. All films had a smooth surface, and no particulates or droplets were observed by optical microscope or SEM, which can be due to the small laser wavelength used for the ablation process, i.e. 248 nm [24]. From EDS line scans (not shown) we found that Cr is randomly distributed, and there are no Cr clusters in the films. The Cr content in the films was in the range x = 2.0–5.0 at.% as determined by RBS. The Cr content and the growth rates are plotted as a function of laser fluence in Fig. 6. We see that both increase with increasing fluence. Note that the growth rate is lower for the film deposited using a smaller laser spot size. From the inset in Fig. 6 we see that the Cr content in the deposited film increases from 3.3 at.% to 4.8 at.% when Np increases from 7000 to 7000. In addition, a higher Np results in lower growth rate.

The XRD patterns of selected films with various Cr contents are shown in Fig. 1(b)–(d). Fig. 1(e) shows the XRD result of the Si substrate. According to the XRD results, all of the films have one main peak at 2θ = 28.6° which can be assigned to both (111) oriented zincblende and (001) oriented wurzite. The XRD peak width(s) (FWHM) of the films with Cr content of 2.0%, 3.3%, and 5.0% determined to be 0.28°, 0.66°, and 0.77°, respectively. Since a lower FWHM of the XRD peak is an indication of higher coherent length of the lattice, inclusion of Cr in the lattice has resulted in additional defects or smaller grain size. In addition, films with Cr content of 3.3 at.% or higher also have a second low intensity peak at 2θ = 27.1° which is assigned to W(100).

For a given fluence, the increase in Cr content with increasing Np is associated with the number of exposed Cr particles (pillars) on the target surface; i.e. the surface ratio of Cr to matrix is increased for higher Np. However, the increase in the number of exposed Cr particles is not linear with increasing Np, and the Cr content approaches a maximum value asymptotically. For the particular target we used, the maximum Cr content in the films (~5 at.%) is reached when a high number of pre-ablation pulses of 2000 pulses per spot were used (performed at φ = 4.5 J/cm²). A semi-stable condition could be achieved after ~22,000 pulses at 3 J/cm² ≤ φ ≤ 4 J/cm², on an area of 1 × 2 cm². Films with nearly constant Cr content (within ±5%) can be deposited for φ = 1–7.8 J/cm², as long as Np > 22,000 and the number of laser pulses needed to deposit the film does not exceed 15,000 pulses. Before each deposition, a polish and pre-ablation process is required to have a reproducible target condition. If a Cr content lower than 2 at.% is desired, another target with lower initial Cr content must be used, although a further decrease of laser fluence may also result in a lower Cr content. The rise in Cr content with increasing laser fluence can have several origins. Firstly, both 4th and the increase in material removal per pulse with increasing fluence are higher for Cr compared to the matrix, i.e. Cr is more sensitive to the fluence for the range of fluences used. In addition to the primary laser ablation process, material can be removed from the target by secondary processes. For instance, a fraction of the ablated material can be back-scattered towards the target surface and may cause sputtering over a larger area than the laser spot size [25]. Such sputtering is more effective at higher fluence since the plasma is more dense and more collisions are expected. Another possible secondary process is preferential re-sputtering of depositing species by the high energy particles in the plume in favor of Cr. This effect also increases with increasing fluence. Finally, the increase in fluence also increases the density of pillars (i.e. exposed Cr particles), which can result in higher ratio of Cr surface to matrix as mentioned above.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Melting point Tm, reflectance R, optical penetration depth l₃, thermal diffusivity D and thermal diffusion length l₅ for ZnS and Cr.</th>
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<tbody>
<tr>
<td></td>
<td>Tm (K)</td>
</tr>
<tr>
<td>ZnS</td>
<td>1973</td>
</tr>
<tr>
<td>Cr</td>
<td>2130</td>
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</table>

a Calculated for λ = 248 nm at incident angle of 45° using data in Ref. [18] (p. 384) and Ref. [19] (p. 611).
b Calculated using l₃ = 0.8 × l₅, (Ref. [17] p. 21), where τ is laser pulse duration time and ζ = 2.
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