Design of ZnSe QPM for Wide Transparency Sensing and Laser Applications

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ABSTRACT

ZnSe has been a great choice for the rare-earth and transition metal doping to develop lasers. It is an excellent material for variety of optical applications due to wide transparency range, good fabricability and very low optical absorption similar to other selenides. NASA Marshall Space Flight Center has developed large crystals using physical vapor deposition (PVD) doped with transition metals for lasing. GaAs based quasi-phase matched structures have a lot of limitations including difficulty of frequency conversion from available high power lasers. We are developing Si- and GaAs- based templates and using microfabrication process to deposit ZnSe using physical vapor transport (PVT) method. Experimental results of the fabrication of templates and growth of ZnSe on templates will be presented.

Keywords: Epitaxial, Zinc Selenide, Gallium Arsenide, Film, Crystal, Quality
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1. INTRODUCTION

ZnSe is an interesting wide bandgap material, which has an excellent potential for light emitting diodes and, in some geometry, can be used for nonlinear optical applications. For these applications, bulk and thin film of this materials have been grown by hydrogen transport vapour phase, open tube transport of elemental vapours and organometallic chemical vapour deposition methods. These methods have been used to grow thin films and in some cases these techniques have been suitable to dope the ZnSe with desired impurities. It is reported that ZnSe dissociates when it is evaporated at high temperature. The sticking coefficients also vary for evaporating species as the temperature changes. There have been many studies in the last thirty years in the area of nonlinear optics since the discovery of the second harmonic generator (SHG) and optical parametric oscillator (OPO). These operations have been achieved through the visible and the infrared spectrum beyond 12 µm. The main obstacle to more widespread use of SHG and OPO concepts has been the difficulty in growing large, high quality nonlinear crystals with a combination of high nonlinear coefficients and optical and mechanical parameters compatible with high average power operation. Although materials such as ZGP are available, only selenide crystals enable us direct conversion from 1.06 to 18 micrometer wavelength region. These materials have shown great promise and are excellent candidates for the systems applications. For this reason large amount of researches [1-6] have been performed to grow bulk crystals of selenides $AgGaSe_2$, Tl_3AsSe_3, GaSe and $Tl_{(3-x)}AsSe_{(3-x)}S_x$ binary solid-solution and bulk and QPM of ZnSe. Similar studies have been performed on self-poled binary halides for the quasi phase matched structure. In continuation of development of the selenide crystals, we have grown several binary materials on GaAs substrate [1,2]. In this paper we report preliminary progress on a new method for the preparation of QPM template using silicon substrates. The quality was analysed by SEM and depth of gratings by chemical etching of the film. We are continuing film grown by physical vapour transport grew hetro epitaxially on Si and GaAs wafers to evaluate suitability of this fabrication process.

2. EXPERIMENTAL METHODS

2.1 Template design and preparation: The template preparation involved the fabrication on the wafer at the micrometer scale. We used microfabrication to design and fabricate [7] gratings of different size width of gratings .and gap width. This fabrication process involves solvent cleaning, deposition of silicon oxide, soft and hard bake, photolithography and development. Both wet and dry etching were used to fabricate the template structures. By combining dry and wet etches, we obtained the desired width and depth of lamella on silicon and gallium arsenide wafers. The steps are given in Figure1.

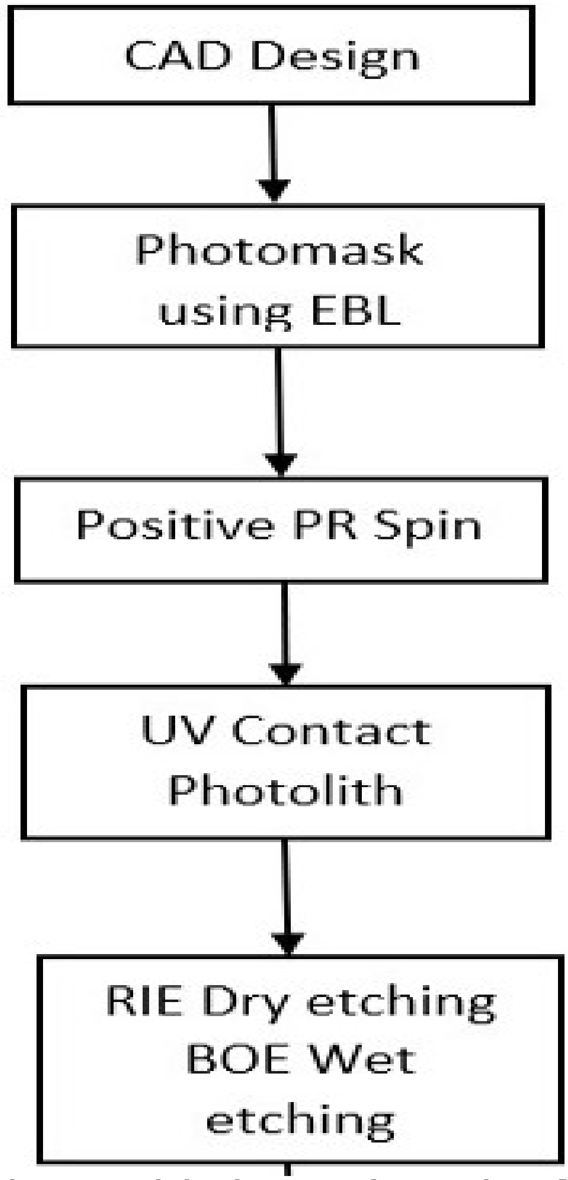


Figure 1. Fabrication steps for templates [7]

2.1 Source Material and Purification: As supplied, ZnSe source material was listed for 99.999% purity. It was further purified by transporting the material under thermal gradient in a well cleaned vacuum-sealed quartz tube [1-2].
2.2 Template cleaning: Si and GaAs Wafers were used for the template fabrication. However, we will report only results of silicon wafers We used 2" and 3" wafers as starting substrates. The surface of the material was prepared by washing the surface with trichloroethylene followed by etching with a mixture of H_2O_2 + H_2O + H_2SO_4 in 1:1:3 ratios followed by rinsing in water. The etching time was 30 seconds. The wafer was dried in vacuum in argon atmosphere.
2.3 Growth of ZnSe on templates: The growth experiment involved substrate preparation, purification of ZnSe source materials and growth under vacuum. Thin film of ZnSe film was grown by physical vapour transport (PVT) growth method in the DENTON evaporator system. We could not control transport path and temperatures by this process. To control growth parameters, we have started design of growth in the closed tube sealed under vacuum. The growth chamber is made of quartz tube. The diameter of this tube is 40 mm. The source temperature is in the range of 600-650 C to achieve different growth conditions. The details of this process is reported in **reference {X]** . The furnace designed to grow ZnSe on template is shown in Figure 2.

2.4 Morphological Characterization: Templates were characterized by SEM was used to evaluate the interface quality and thickness. AFM is a Veeco model D3000 SPM was used to determine the 2D and 3D surface morphology of films with different thicknesses. Results from scanning electron microscopy (SEM) to examine the shapes of the fabricated arrays are presented in this study.

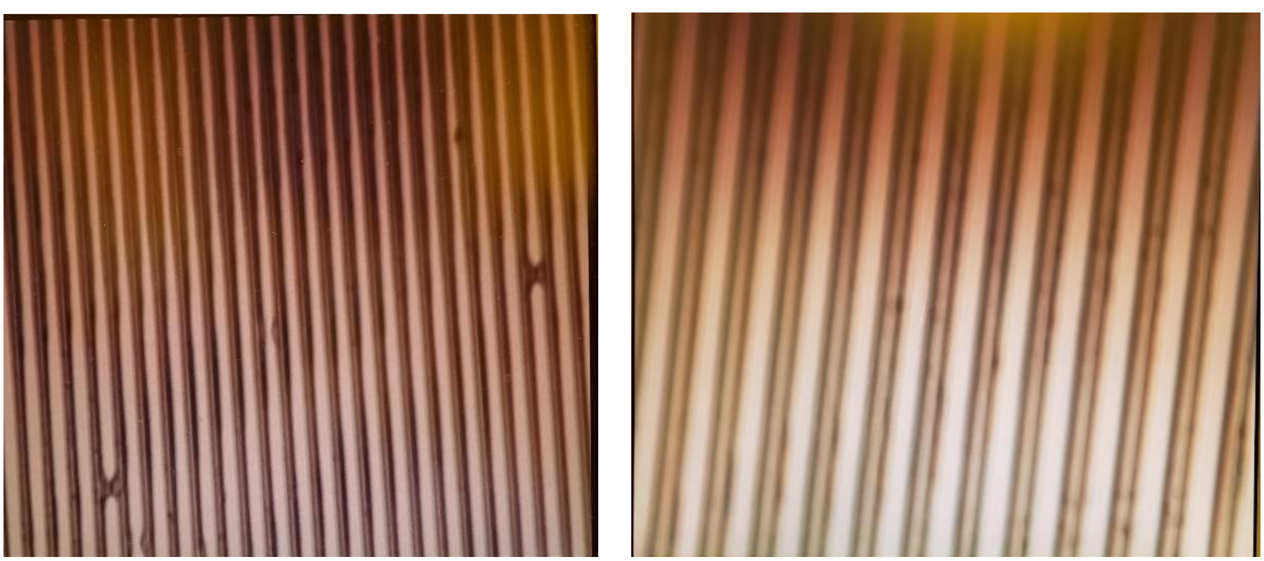
Figure 2. A two zone gold coated furnace for physical vapor transport of ZnSe on templates. Each zone is controlled by separated controllers independently

3. RESULTS AND DISCUSSION

The colour of the purified ZnSe was bright orange. Materials prepared by similar process did not was characterized by X-ray diffraction patterns and micro probe which did not show **[X]** any major impurity in the purified ZnSe material. We had not observed oxygen impurity in the material. During the evaporation process, great care was taken for the quartz cleaning, drying and annealing to avoid contamination of ZnSe. During the bulk ZnSe growth we had observed **[X]** that rough surfaces on the wall of the growth tube could be a source of impurity especially in high temperature growth conditions. The texture and the colour of the film did not change a lot. It was always amber. A photomask is a quartz or glass substrate, coated with an opaque film was used. It was designed to optically transfer patterns to wafers substrate. The lamella patterns information was created in the AutoCAD tool. The design was reformatted into internal CAD format and transfer to E-beam writer which exposed the design onto the photomask substrate. Photomask fabrication involves many steps such as data preparation, exposure, chrome process, etching, stripping and photomask cleaning as shown in Figure 1 [7]. Data preparation translated the set of different size templates onto the set of instructions that photomask writers used to generate the physical mask. Figure 3 shows a QPM template designed on silicon wafer with multiple gratings.

Figure 3. A multi spacing QPM design for silicon wafer

The detailed examination using SEM for each size grating indicated that templates with smaller sizes (35 μm) had some defects as precipitates on the lamella. Figure 4 (a) shows these defects. However, as shown in Figure 4(b) we did not observed precipitates and further improvement is possible. When depth was increased in these gratings we observed more defects as shown in Figure 6



(a) **(b)**

Figure 4. A grating with 35 micrometer spacing. (a) showing some precipitates and (b) no sign of precipitate of voids.

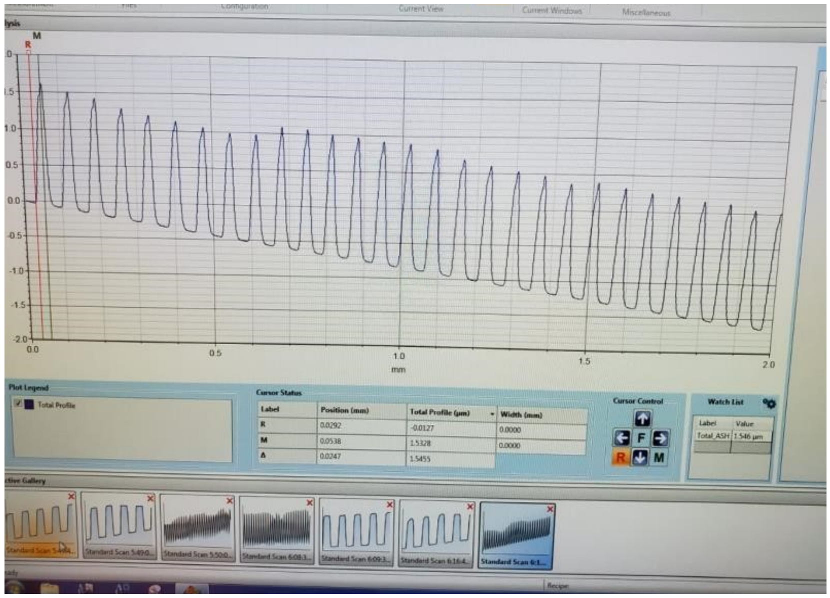


Figure 5. Depth of 35μm gratings on wafer

Figure 6. Defects were observed in the middle as well as at the edges of the lamella.

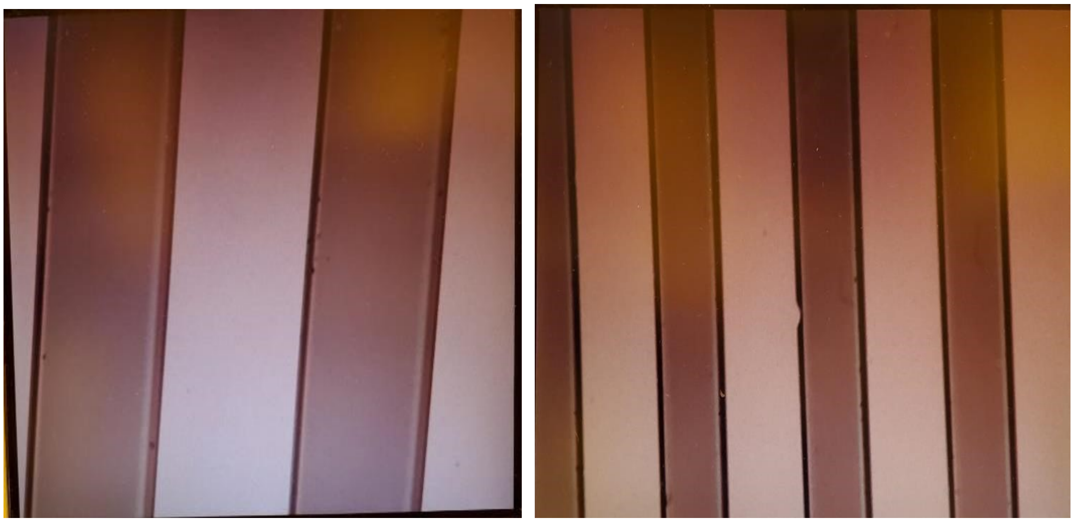


Figure 7. No defects were observed on 230μm gratings

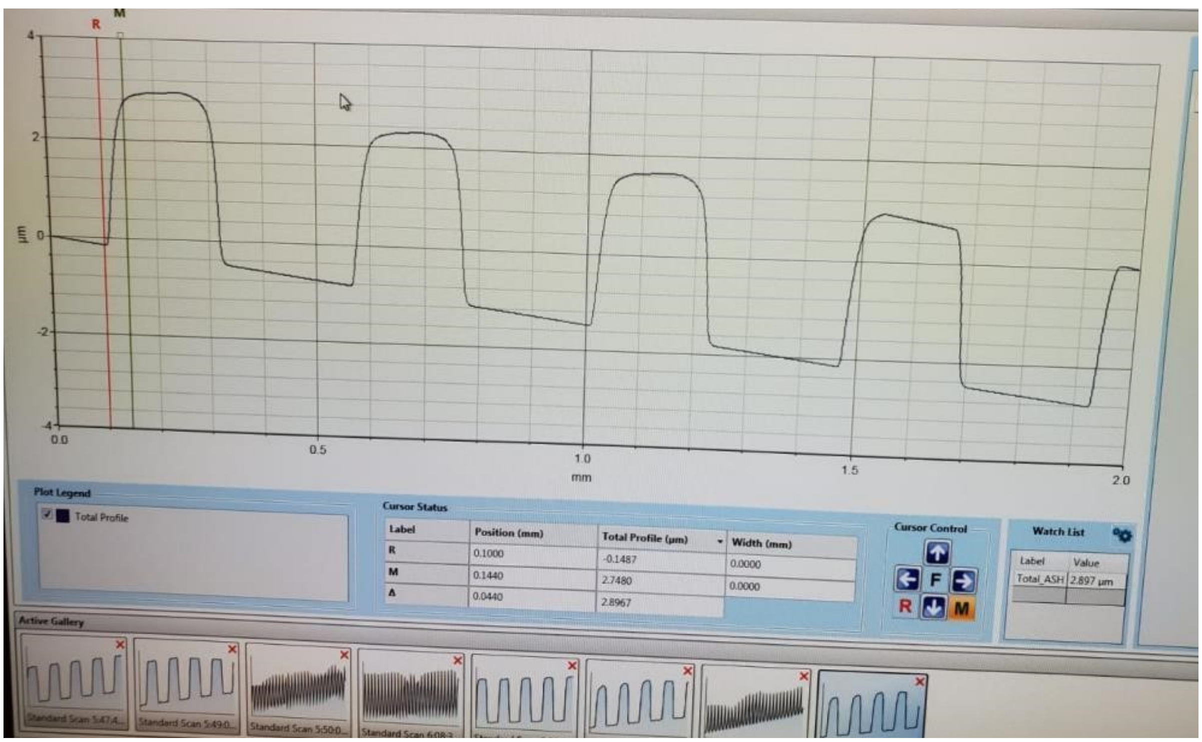


Figure 8. Depth of 230μm gratings on wafer

We have several growth test runs on the Si wafers based templates. We are still characterizing these templates. Although there is no comprehensive data on the lattice parameters of the fabricated templates in the 500 to 650C we expected highly heteroepixaial film on the templates. This situation will be different since the lattice parameters of GaAs and ZnSe can be matched and better homoepitaxial films are possible. Also, Czerniak and Lilley **[5]** and Scott, Williams and Goodfellow [**6]** have described the details of kinetics of ZnSe growth. However, most of these methods used iodine or other carrier gases to enhance the growth speed. Our objectives are to develop low cost templates and grow undoped high purity and we used only thermal gradient as the driving force and did not use a carrier gas. As it is well known, control of transport path length, substrate and source temperature (ΔT_H - ΔT_C), and the orientation of the substrate with respect to vapour transport in DENTON is very difficult, we could not get thick good quality films. We have already designed furnace and quartz ampuls where T_H, T_c, diameter of transport and path length can be controlled for future ZnSe growth runs in this furnace.

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4. SUMMARY

The quality of the quasi-phase matched growth of ZnSe is very much dependent on the quality and availability of low cost templates. We present a novel approach for fabrication of templates. In this paper we report the preliminary results of the steps and challenges if fabrication using silicon wafers. The modification of etching showed improvements in 35 and 250 mm range gratings with depth suitable to control the growth of ZnSe.

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