LASER-INDUCED OXIDIZED ZINC ALLOY FILMS FOR DIRECT-WRITE GRAYSCALE PHOTOMASKS

By

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In the School of Engineering Science

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## APPROVAL

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ABSTRACT

Previous research showed laser-induced oxidization in Bi/In and Sn/In bimetallic films produced a large optical density change (3.00 to 0.22 OD at 365nm), making them promising in grayscale photomask application. This thesis explores Zn alloys as new bimetallic combinations. Sn/Zn, Zn/Sn, Al/Zn, Zn/Al, Bi/Zn, Zn/Bi and In/Zn were DC/RF-sputtering deposited and then exposed to an argon ion CW laser (spot size ≤ 10μm). Using a UV/visible spectrometer, the most transparent material obtained was an exposed In/Zn film (3.20 to 0.20 OD). Zn/Sn, Zn/Al and Sn/Zn, producing a shallow OD versus laser power slope (5~9 OD/W) over a 0.4W power range while achieving a large OD range up to 3.45, gave the best results for laser direct-write grayscale photomasks. These bimetallic photomasks are able to pattern complex 3D microstructures by a single exposure. Using UV photolithography with these grayscale masks and SU-8 photoresist, 100μm high microbridges and 30°~60° V-grooves were fabricated.

Keywords: grayscale photomask; laser; zinc alloy; UV photolithography

Subject Terms: Grayscale photomasks for microfabrication
DEDICATION

To my husband, Song Xue, and my daughter, Lan Xue,
for their understanding and support
during this degree pursuit.
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To them, I dedicate this thesis.
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<td>BZO</td>
<td>Bismuth doped ZnO</td>
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<td>LEDs</td>
<td>Light-Emitting Diodes</td>
</tr>
<tr>
<td>MEMS</td>
<td>Micro-Electro-Mechanical-Systems</td>
</tr>
<tr>
<td>MOEMS</td>
<td>Micro-Opto-Electro-Mechanical-Systems</td>
</tr>
<tr>
<td>OD</td>
<td>Optical Density</td>
</tr>
<tr>
<td>RAT</td>
<td>Reflection, absorption and transmission</td>
</tr>
<tr>
<td>RF</td>
<td>Radio Frequency</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>Acronym</td>
<td>Full Form</td>
</tr>
<tr>
<td>---------</td>
<td>-----------</td>
</tr>
<tr>
<td>SOG</td>
<td>Spin-On-Glass</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning Transmission Electron Microscope</td>
</tr>
<tr>
<td>TCO</td>
<td>Transparent Conductive Oxide</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
</tr>
<tr>
<td>TFT</td>
<td>Thin Film Transistors</td>
</tr>
<tr>
<td>TZO</td>
<td>Tin doped ZnO</td>
</tr>
<tr>
<td>UV</td>
<td>UltraViolet</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
</tbody>
</table>
CHAPTER 1. OVERVIEW

1.1 Introduction

A photomask is a template whose transparency levels control the light applied to a photosensitive surface. It enables photolithography to create precise microstructures in Integrated Circuits (ICs) and thus has become a significantly important part of the semiconductor production industry [1]. Recently, because of strong growth in the semiconductor market, photomask sales have grown dramatically. According to The Information Network [2], the recorded growth of the photomask merchant market is 17.9% in 2004, 7.8% in 2005 and 5.4% in 2006, with an expected gain of 7% in 2007.

Photomasks play a determining role in the size, shape and quality of IC components [3] [4] [5]. In fact, current photomask research is being stimulated to keep pace with the semiconductor market’s growing demands for microfeature complexity at reduced costs [1] [6].

This thesis explores a promising new photomask fabrication technology, developed at SFU, using several novel materials for creating thin film photomasks that have many unique characteristics not possessed by traditional masks. In this first chapter of the thesis, photolithography technology and the limitations of commercial photomasks are reviewed. This overview enables an understanding of the objective of this research, which is stated at the end of this chapter.

1.2 UV Photolithography

Photolithography, also referred to microlithography or optical lithography, is the set of steps used for transferring geometric patterns from a photomask to a thin photosensitive layer (photoresist). The design is then reproduced on a substrate layer lying below the photoresist [7].

A photolithographic system includes a photomask plate, a photoresist layer and an exposure apparatus [8]. The masks explored in this thesis are used in UltraViolet (UV)
photolithography, many of which use the 365nm wavelength (I-line) from a high-pressure Hg or Hg-rare gas discharge lamp [8]. Nowadays, to achieve high resolution, new lithographic technologies with even shorter wavelength sources are used, such as Deep UltraViolet (DUV) using 248nm or 193nm light from excimer lasers and Extreme UltraViolet (EUV) using 13.5nm light source. However, traditional UV photolithography is still used in mass production lines in conjunction with those new technologies [1] [5] [9].

The conventional UV photolithographic process includes photoresist coating, soft-bake, UV exposure, hard-bake, developing, etching and photoresist striping. A typical photolithographic process [10] is shown in Figure 1-1.

![Illustration of a typical photolithographic process](image)

Figure 1-1. Illustration of a typical photolithographic process

First, as shown in Figure 1-1(a) and Figure 1-1(b), a photoresist layer is spun on top of a cleaned substrate (e.g., a silicon wafer). Then, after a soft-bake to evaporate solvents, the photoresist layer is selectively illuminated through the photomask during the exposure step (Figure 1-1(c)), changing the solubility properties of the exposed photoresist. During the development step (Figure 1-1(d)), the photoresist is partially removed by developer solution. For positive photoresist, the illuminated part is removed (Figure 1-1(e)), but for negative photoresist, the illuminated part remains after the development step. A hard-bake step is performed after developing in order to harden the photoresist and improve the adhesion of the photoresist to the substrates. Then, the
uncovered thin film below the photoresist layer is etched away using a chemical treatment (Figure 1-1(e)). Finally, a photoresist strip process removes the resist pattern (Figure 1-1(f)), creating a copy of the photomask pattern on the substrate.

In modern processes, an IC fabrication requires up to 30 successful deposition and photolithographic steps. The complexity of an IC process is often measured by the number of the photomasks involved during fabrication [8]. Depending on the application, photomasks can be divided into either binary or grayscale photomasks.

1.3 Binary Photomasks

A photomask, whether binary or grayscale, has a transparent substrate (e.g., glass, plastic or quartz) and a patterned absorbing layer (e.g., metal). The typical structure of a binary mask is chromium on a quartz plate, which fully blocks or clearly illuminates the photoresist (see Figure 1-1(c)). Binary photomasks play a significant role in creating 2D structures and, for several decades, they have been widely applied in the fabrication industry for creating ICs layouts. Grayscale photomasks, on the other hand, have many transparency levels within a single template. They are most often used for producing complex three-dimensional structures with continuously-varied heights, such as Micro-Opto-Electro-Mechanical-Systems (MOEMS).

For both binary and grayscale photomasks, the optical density is the most significant parameter, which is expressed by transmittance $T$ (0–100%) using the following equation:

$$ OD = -\log_{10}(T) \quad \text{(1-1)} $$

where $OD$ and $T$ are wavelength dependent.

Figure 1-2 shows the transmittance and its corresponding calculated OD of a glass slide (Pearl® CAT No. 7101) which was used as a substrate for our thin film mask. As the light range moves from DUV to visible light, the transmittances of the glass slide increases, meaning the OD decreases. At 365nm, the transmittance is 84.3%, corresponding to 0.07 OD. In this research, the photomask’s OD values at 365nm are the most interesting because of their common usage in some UV photolithographic processes.
As shown in Figure 1-1(c), the ideal binary mask acts as a light switch, either completely impeding light or completely transmitting. Ideally, the light transmission is either 100% or 0%. However, for a typical binary photomask at 365nm, the transparency of a practical chrome absorber on a quartz plate is around 0.1% (3.0 OD) [1].

![Graph showing transmittance and OD curves](image)

*Figure 1-2. A glass slide (Pearl® CAT No. 7101) transmittance curve versus wavelength (left) and the corresponding OD curve versus wavelength (right)*

### 1.4 Grayscale Photomasks

The ability of photolithography to produce 3D structures with arbitrary shapes is of increasing importance in the miniaturization of micro-mechanical devices, micro-fluidic devices, micro-optical elements, and self-assembling components [11] [15]. Because grayscale photolithography is an inexpensive one-step lithography process capable of fabricating well-defined curved surfaces, it attracts considerable attention.

Grayscale photomasks require more transmittance levels within a single template than binary photomasks, allowing masks to create more complex structures in grayscale photolithography than binary photomasks. Figure 1-3 (a) shows that the light passing through the grayscale pattern has various intensities; therefore, the resist is activated by varying dosages of light. The different exposure amount in the photoresist creates different levels of solubility to the developer. Assuming the photoresist in Figure 1-3 is positive photoresist, the amount of photoresist removed during development is proportional to the exposure amount. Therefore, the stronger illumination of the resist,
the thinner the thickness left after development (Figure 1-3 (b)). Then, during dry plasma etching, the rate and amount of the lower layer that is removed depends on the above photoresist thickness. Ideally, the etching is adjusted so the rate at which photoresist removed is the same as the etch rate of the substrate. In the end, the resist pattern, which reveals the transmittance distribution of the mask, is transferred to the substrate layer below (Figure 1-3(c)). Therefore, a mask with more transmittance levels allows the creation of structures with greater height variations and higher complexities.

![Figure 1-3. Mechanism of grayscale photomask applied in the photolithographic process](image)

1.4.1 Classification of Grayscale Photomasks

Grayscale photomasks are divided into either binary halftone or analogue continuous tone grayscale masks. Figure 1-4 shows the difference between a binary mask (Figure 1-4(a)) and an analogue grayscale pattern (Figure 1-4(b)) when applied to the same mountain scene. The continuous tone grayscale pattern shows much greater grayscale details, with smoother transition than the halftone image, in which discontinuities are obvious, especially in its enlarged image (Figure 1-4(c)). In binary grayscale masks, variable dot sizes and dot densities produce different transmittance distributions. By defocusing this image, the chrome halftone binary photomask generates grayscale exposure levels in the photoresist. However, the available grayscale levels in a typical halftone mask are limited to 16 levels [14].

Halftone-created-images also suffer from the Moiré effect, which are interference patterns created in the resist by the interaction between different dot density areas on the masks. Moreover, the high exposure light source required for defocusing results in the rapid degradation of the masks [17] [18].
Analog grayscale photomasks, on the other hand, enable a single exposure to create complex 3D structure in photoresist. Based on the reasons above, analog grayscale technology is receiving more interest over digital binary grayscale technology, especially in microfabrication applications for structures with smooth and continuously-shaped surfaces. The increasing demand for complex 3D microstructure fabrication has stimulated the research and development of grayscale masks. Some methods for creating high resolution analog grayscale masks are ultra-high resolution halftone photomasks [1], Microfluidic photomasks [11], Spin-On-Glass (SOG) photomasks [15], varying-height metal-on-glass photomasks [11] and High Energy Beam Sensitive (HEBS) glass [16]. However, only the analogue grayscale mask using HEBS glass is commercialized.

1.4.2 HEBS Analog Grayscale Photomasks

HEBS glass is used in the most successfully commercialized analogue grayscale photomask [16]. The transmittance created in HEBS glass is controlled by dosage of an e-beam. HEBS glass is silver doped and it starts as transparent and reacts to the e-beam by becoming darker. The e-beam, therefore, is capable of writing grayscale patterns into HEBS glass. This direct-writing technology simplifies the mask’s manufacturing process,
but it increases the cost. Although this method achieves more grayscale levels (up to 50), it heavily absorbs wavelengths shorter than 330nm (e.g., DUV). At the I-line wavelength 365nm, HEBS has only a 1.2 OD range (from 1.4 OD to 0.2 OD), resulting in 3D structures transferred from the HEBS glass that have very limited height-variation and shape-complexity.

1.5 Bimetallic Grayscale Photomask

Recent research at Simon Fraser University demonstrated that an alternative to traditional grayscale photomasks is laser direct-write Bi/In and Sn/In bimetallic films that can create grayscale photomasks with a simpler and cheaper process while having a much larger OD range \([20][21][22][23][24][25][26][27]\). These unique characteristics suggest a promising future in UV photolithography and other applications.

1.5.1 Optical Properties

As shown in Figure 1-5, for this alternative process, a two-layer structure is made from Bi/In and Sn/In bimetallic films, 15–50 nm in thickness.

![Figure 1-5. Typical structure of a bimetallic Bi/In film](image)

Bi and In or Sn and In have at least one eutectic point, which is a melting point lower than either of the melting points of the two metals and at which the two metals become a stable alloy \([31] [52]\). These eutectic points require low energy for the two metals to form a stable alloy, so the composition of the eutectic point was used to determine the layer thickness of the two metals. Using a sputter deposition process, the thickness of each layer can be well controlled. Following the sputtering on transparent
substrates, the films were patterned using an argon ion CW laser (488nm). The original opaque films were changed to highly transparent after the laser scanning process. The OD of Bi/In and Sn/In typically changes from 3 OD before laser exposure to 0.2 OD after laser exposure.

The exposed Bi/In and Sn/In films show a change in OD that is a function of the writing laser power. Figure 1-6 demonstrates the typical OD versus laser power curve of Bi/In (40/40nm) [29] [30]. Every curve can be divided into three zones. In zone I, the OD of the film shows no change when scanned with a power less than the threshold value. With increasing power, the OD dramatically decreases, as shown in zone II. Then, in zone III, the film is saturated with laser scanning and the OD of the exposed area is the same, even at stronger powers.

![Figure 1-6. OD change with laser power of a 40/40nm Bi/In film](image)

Among these three regions, only the laser range of zone II is useful in the laser direct-write process for grayscale pattern creation. To achieve fine writing control of the film transparency, the variation of the OD and laser power in zone II should be as large as possible. Generally, as shown in Figure 1-6, the laser coverage in zone II is less than 0.1W for a 2 OD range, which shows a slope steeper than 0.05 W/OD. This non-linear relationship of OD versus laser power makes precise control of the laser writing process at some grayscale levels difficult on Bi/In and Sn/In films.
1.5.2 Oxidation Process

Transmission Electron Microscopy (TEM) (Hitachi 8000) analysis was used in previous research [20] [21] to discover that laser scanning on Bi/In and Sn/In bimetallic films involves an oxidation process. Figure 1-7 [20] shows TEM electron diffraction patterns of a Sn/In (12/12nm) film. The film was DC-sputtered on Lacay-Carbon-coated-formvar TEM 300 copper mesh grids. Then, for a short duration (4ns), a single pulse Nd:YAG laser at 532nm (2\textsuperscript{nd} Harmonic) with low power (less than 1 mJ/cm\textsuperscript{2}) was applied to expose the film. This short pulse prevented the formvar carbon layer from being damaged.

![Figure 1-7. TEM Electron diffraction patterns of (a) as-deposited Sn/In film and (b) exposed Sn/In film](from Jun Peng, 2006, SFU thesis, Figure 5.11 [20], by permission)

After TEM analysis, the crystal structures in the TEM patterns were labelled based on calculations and comparisons with the JCPDF x-ray diffraction pattern [20]. Comparing Figure 1-7 (a) to (b), after laser exposure, electronic diffraction rings of oxides appeared. These results demonstrate that OD reduction at the exposed areas is caused by transparent oxides rather than material removal or laser ablation.

1.6 Thesis Objective

The previous work on Bi/In and Sn/In bimetallic films is the foundation of this thesis research. Although these two alloys have a large OD range at 365nm compared to conventional grayscale photomasks, the rapid OD response to laser power makes their precise control of the laser direct-writing on some grayscale levels difficult. A grayscale
material that can achieve 256 grayscale levels is desired for manufacturing. This thesis research explored new materials for laser direct-write grayscale masks. Zn and Zn alloy thin films were investigated as candidates for creating practical laser direct-write grayscale photomasks at a reduced cost.

The complete oxidation of zinc and zinc alloys has been investigated [57], but zinc’s partial oxidation for grayscale masks has not been explored yet. In this research, partially oxidized zinc, indium zinc alloy, tin zinc alloy, bismuth zinc alloy and aluminium zinc alloy films were studied as candidates for improved grayscale photomasks. Furthermore, the practicalities of these Zn alloy masks were explored for 3D microstructures fabrication in SU-8 with UV photolithographic processes.

1.7 Summary

The increasing number of applications for photolithography manufacturing continues to stimulate intense research about photolithographic equipment and components. Because photomasks are the design limiting factor in IC microfabrication, their progress can significantly improve semiconductor fabrication technology. In this thesis, ZnO-based direct-write grayscale photomasks were developed as an alternative to conventional photomasks.

Chapter 1 introduced background information of this research, from UV photolithography to current commercialized grayscale masks. The previous work on Bi/In and Sn/In was the basis of this research and thus was emphasized.

Chapter 2 presents the properties of ZnO and the considerations for the new bimetallic combination. Then the theoretical analyses about optical and thermal properties of these materials using computer simulations are introduced. An optical model calculates the optical absorption characteristics for Zn and Zn bimetallic films with a thickness up to 100 nm. The thermal modelling simulates the heat flux and temperature distribution by laser radiation on films.

Chapter 3 describes the fabrication steps and the equipment used for measuring the exposed films. A UV/visible spectrometer, microscope, profilometry, X-ray
Diffraction (XRD), and Energy-Dispersive X-ray (EDX) spectroscopy were used to characterize the composition, profile and optical density of the exposed films.

Chapter 4 discusses the results for the material and surface analysis of the exposed Zn and Zn bimetallic films. All the analyses demonstrate that the laser direct-imaging in these metal thin films involves, but is not limited to, an oxidizing process. At the end of this chapter, all the films are compared for their capacity to be laser direct-write grayscale masks.

Chapter 5 shows the practical application of these thin films in standard UV photolithography. Complex 3D microstructures patterned by these thin film masks were created in SU-8 photoresist. These microstructures presented the quality of the mask patterns created in the thin films.

Finally, Chapter 6 provides conclusions and future work of this research.
CHAPTER 2. THEORY OF SIMULATIONS FOR ZNO-BASED PHOTOMASKS

2.1 Introduction

Although previous research shows that Bi/In and Sn/In have many advantages as grayscale photomasks materials, the OD of these two films changes rapidly with laser power in the middle of the OD range. This steep slope makes controlling the grayscale laser direct-writing in that grayscale range difficult. Therefore, finding new metal combinations has become a goal for this investigation. In this research, Zn and Zn alloy thin films were explored as candidates for improved laser direct-imaging grayscale photomask materials.

First, the general properties and applications of ZnO are discussed along with an investigation of the oxidation process of Zn. Next, simulations for the light absorption ability and heat flow during laser illumination are presented.

2.2 ZnO-Based Materials

Zinc is a bluish-white, lustrous metal with a melting point of 419.53°C, which is much higher than our previously studied materials: bismuth (271.43°C), indium (156.60°C) and tin (231.93°C) [31]. Compared to those three metals, zinc has a wider range of temperatures before it melts.

Zinc is not considered to be toxic [31] and it is one of the most extensively used metals in automotive, electrical, and other industries. Zinc can form numerous alloys with other metals.

2.2.1 Applications and Properties of ZnO

ZnO is a transparent, n-type semiconductor with a large bandgap of 3.2eV (at room temperature) [31] [38] [39]. It is non-toxic, economical, stable, and has high transparency in the visible range. ZnO can be formed into crystals, powder and thin films.
with high stability [31]. Table 2-1 summaries the key features of ZnO in wurtzite and sphalerite structures [31]. Wurtzite is a hexagonal crystal system, consisting of tetrahedrally coordinated zinc and sulphur atoms [32]. Sphalerite is a chief ore of zinc, which consists of zinc sulfide and iron [33]. Like wurtzite, sphalerite is also closely related to the structure of diamonds.

Table 2-1. Basic properties of ZnO [31]

<table>
<thead>
<tr>
<th>Property</th>
<th>Sphalerite Structure</th>
<th>Wurtzite Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>81.4</td>
<td>81.4</td>
</tr>
<tr>
<td>Average atomic weight</td>
<td>40.7</td>
<td>40.7</td>
</tr>
<tr>
<td>Lattice parameters (Å) (300K)</td>
<td>4.6</td>
<td>3.2, 5.2</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>5.7</td>
<td>5.7</td>
</tr>
<tr>
<td>Melting point (K)</td>
<td>2248.0</td>
<td>2250.0</td>
</tr>
<tr>
<td>Specific heat (J/Kg.K) (300K)</td>
<td>494.0</td>
<td>—</td>
</tr>
<tr>
<td>Debye temperature (K)</td>
<td>416.0</td>
<td>—</td>
</tr>
<tr>
<td>Coefficient of thermal linear expansion (10⁻⁶/K) (300K)</td>
<td>2.9</td>
<td>—</td>
</tr>
<tr>
<td>Thermal conductivity (mW/cm.K) (300K)</td>
<td>234.0</td>
<td>600.0</td>
</tr>
<tr>
<td>Heat of formation (kJ/mol) (300K)</td>
<td>-350.0</td>
<td>-350.0</td>
</tr>
<tr>
<td>Minimum room temperature energy gap (eV)</td>
<td>3.2</td>
<td>3.2</td>
</tr>
<tr>
<td>Electrons mobility (cm²/Vs) (300K)</td>
<td>180.0</td>
<td>180.0</td>
</tr>
</tbody>
</table>

ZnO possess very good photoconductivity and luminescence properties. It is widely used in electro-acoustic transducers, photovoltaic conversion of solar energy, optoelectronic displays, electro-photography and gas sensors [34] [40]. Even though the study of ZnO began in 1935, the current renewed interest follows the growth of technologies for fabricating high quality single crystals and exipitaxial layers, which extends the application of ZnO-based electronic and optoelectronic devices [34].

In particular, ZnO has been extensively studied because of commercial applications in phosphors, Light-Emitting Diodes (LEDs), Laser Diodes (LDs), piezoelectric transducers, and transparent conducting films [35] [36] [37] [38]. The very recent improvements in growing p-type ZnO material[34] [41] [42] indicates its promise for creating transparent Thin Film Transistors (TFT) with a plastic or flexible substrate material, allowing ZnO to be a part of many functional and exotic devices.
2.2.2 Bandgap Wavelength of ZnO

The optical properties of ZnO are the most interesting for this research. As shown in equation 2-1, the bandgap wavelength is inversely proportional to its corresponding bandgap:

$$\lambda = \frac{1239.8}{E_g},$$

where $\lambda$ is the bandgap wavelength in nm and $E_g$ is the bandgap energy in eV.

Using a bandgap value of 3.2eV in this equation, we find that the corresponding wavelength of pure crystal ZnO is 387nm, which means that ZnO highly absorbs light shorter than this wavelength. For UV exposure systems, the common light source Hg-Xe lamps have peaks (e.g., I-line) below ZnO bandgap wavelength; thus, pure crystal ZnO is not transparent to I-line. This result may narrow its application for masks in the UV photolithographic aligner.

However, the bandgap can be shifted by either the preparation process or the composition of certain semiconductor alloys [55] [43]. In this research, several metals were chosen to form different Zn alloys in an attempt to shift the bandgap wavelength of the ZnO to a value lower than 365nm after laser exposure process. We first took into account the metals used to form Zn alloys, and then the corresponding ratios of these bimetallic films were considered.

2.2.3 Alloy Materials

As an economical transparent oxide, ZnO exhibits good optical and electrical properties with lower costs compared to Indium Tin Oxide (ITO) [36] [50]. Of most interest is the research on dopants to form ZnO-based amorphous and crystalline materials for TCO applications. Aluminum doped ZnO (AZO) [36], Tin doped ZnO (TZO) [44], Indium doped ZnO (IZO) [35] [37] [45] [46] and Bismuth doped ZnO (BZO) [51] have extensively enhanced pure ZnO’s application for high-quality TCO and related devices. These materials also possess very stable properties and have a wide range of applications for visible transparent doped-ZnO materials. Therefore, for this thesis, tin, aluminium, bismuth and indium dopants were considered.
To obtain a better UV transparency than pure ZnO, a wider bandgap energy for each suggested metal oxide is needed. Tin oxide’s bandgap energy is 3.4eV~4.6eV and so its bandgap wavelength is 364~270nm [44], indium oxide’s bandgap energy is 3.6eV at 344nm bandgap wavelength [45] [46] and aluminium oxide’s is 8eV at 155nm [47] [48]. One of the advantages of using In, Al, and Sn is that they can shrink the bandgap wavelength of these ZnO-based materials. For instance, the bandgap of IZO is 3.88eV with a 319nm bandgap wavelength, AZO has a 350nm bandgap wavelength [49] and ITO has a bandgap of 3.5~4.3eV and, therefore has a 354~290nm bandgap wavelength [50]. In comparison to pure Zn film, adding In, Sn and Al into a pure zinc films to form Zn alloys after laser-induced oxidation was expected to have a higher transmittance at 365nm.

Nevertheless, bismuth oxide only has a 2.7eV bandgap, so its bandgap wavelength is 459nm [51], which will block the I-line wavelength. Bismuth was still listed as one of the dopants for this study because bismuth is one of the elements used in the Bi/In thin film grayscale photomasks in earlier studies. Based on the reasons above, In/Zn, Al/Zn, Sn/Zn, and Bi/Zn were chosen for this project.

### 2.2.4 Composition Ratio

In the thesis, a two-layer structure was used for the Zn bimetallic films. Each bimetallic film was named using the symbols of the two corresponding elements with the top layer material showing before a ‘/’. The symbol ‘at. %’ represents the atomic ratio in each alloy. For example, In/Zn (50/50nm with 63 at.% Zn) means that the top layer, t_in, is 50nm of indium and the bottom layer, t_zn, is 50nm of Zn. The corresponding atomic ratio of Zn in this alloy is 63%. The structure of this bilayer film is shown in Figure 2-1.

![Figure 2-1. Diagram of a typical bimetallic thin film structure (In/Zn used as an example)](image_url)
In order to choose the ratio of Zn in each alloy, the corresponding binary phase diagrams shown in Figure 2-2 were investigated [52].

![In-Zn](image1)

![Sn-Zn](image2)

![Al-Zn](image3)

![Bi-Zn](image4)

Figure 2-2. The binary phase diagrams of Zn with In, Sn, Al and Bi (after W. G. Maffatt) [52]

As summarized in Table 2-2, the binary phase diagrams for the four Zn alloys contain at least one eutectic point, which represents the minimum melting point to form the alloy. Note that the eutectic point of each alloy [31] [52] is below the melting point of either metal. The eutectic points are important for the alloys because these are the lowest temperatures at which the alloy can form. In addition, alloys with a eutectic composition ratio are usually very stable. Therefore, we will refer to these specific ratios when we choose the materials and their percentages to form the zinc alloys.

<table>
<thead>
<tr>
<th>Table 2-2. Melting temperature of Zn and Zn alloys [31] [52]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single metal</td>
</tr>
<tr>
<td>Melting point(°C)</td>
</tr>
<tr>
<td>Zn alloy</td>
</tr>
<tr>
<td>Eutectic point(°C)</td>
</tr>
</tbody>
</table>
In this research, these four Zn bimetallic films, with ratios close to these eutectic points, were investigated. Table 2-3 summarises the various parameters.

<table>
<thead>
<tr>
<th>Thin film material</th>
<th>Zn</th>
<th>Al, Zn</th>
<th>Bi, Zn</th>
<th>Sn, Zn</th>
<th>In, Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total thickness(nm)</td>
<td>100-240</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Zn volume ratio (%)</td>
<td>100.0</td>
<td>95.0</td>
<td>3.0</td>
<td>10.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Zn weight ratio (%)</td>
<td>100.0</td>
<td>98.0</td>
<td>2.2</td>
<td>9.7</td>
<td>4.8</td>
</tr>
<tr>
<td>Zn atomic ratio (%)</td>
<td>100.0</td>
<td>95.4</td>
<td>6.7</td>
<td>16.5</td>
<td>8.2</td>
</tr>
<tr>
<td>Zn eutectic volume ratio (%)</td>
<td>88.2</td>
<td>3.6</td>
<td>7.8</td>
<td>2.3</td>
<td></td>
</tr>
</tbody>
</table>

2.3 Optical Absorption Simulation

We simulated the optical properties of the bilayer thin films with different thicknesses. We calculated the reflection ($R$), absorption ($A$), and transmission ($T$) of laser light at 488 nm in thin films on glass slides. The 488 nm wavelength is the same wavelength used in our current laser writing system.

Assuming the incident light is normal to a smooth and flat film surface. The definition of $R$, $A$ and $T$ is given by equation 2-2 and 2-3. These three variables meet the energy conservation law.

\[
R = \frac{I_R}{I_0}, \quad A = \frac{I_A}{I_0}, \quad T = \frac{I_T}{I_0},
\]

\[
R + T + A = 1,
\]

where $I_0$, $I_R$, $I_T$ and $I_A$ are the incident light intensity, the reflected light intensity, the transmitted intensity, and the absorbed intensity, respectively.

An optical model for absorbing bimetallic films was developed by Dr. Glenn H. Chapman and Dr. Marinko V. Sarunic [25] [28]. Based on the Airy summation, this model gives the reflection and transmission at every interface, and the energy that is deposited in the film as a function of the thickness [21]. The result of this optical modelling provides the characteristics of the optical absorption of films with different thicknesses. The detailed mechanism is explained in the literature and the accuracy of this model was confirmed by comparing published results [21] [25] [28].
Unlike most of other optical models, this model is for multilayer materials with high absorbing characteristics [21]. The refractive index, a complex number \( n \), is described by [53],

\[
n = n + ik,
\]

where \( n \) is the real part of the refractive index and \( k \) is the extinction coefficient [31]. The symbol \( k \) represents the fraction of light lost to absorption per unit distance in a participating medium, and it is wavelength dependent [54].

For a fully transparent material, \( k \) equals zero. For a high absorbing material, the value of \( k \) is large [21]. The refractive index, \( n \), and absorption index, \( k \), of Zn, Al, Bi, In and Sn are shown in Table 2-4 [21] [31].

Table 2-4. Refractive index and absorption index at 488nm for various materials [21] [31]

<table>
<thead>
<tr>
<th></th>
<th>Zn</th>
<th>Al</th>
<th>Bi</th>
<th>In</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>0.607778</td>
<td>0.73177</td>
<td>1.877188</td>
<td>0.740150</td>
<td>1.414962</td>
</tr>
<tr>
<td>k</td>
<td>3.449418</td>
<td>5.935573</td>
<td>2.613534</td>
<td>4.813158</td>
<td>4.014286</td>
</tr>
</tbody>
</table>

Using the \( n \) and \( k \) values of each material (air, two metals, and glass), the \( RAT \) (reflected \( R \), absorbed \( A \), and transmitted \( T \) intensity) relationship with film thickness can be plotted. Figure 2-3 to Figure 2-12 give the simulation results of \( RAT \) curves at 488nm laser light with a thickness variation on pure Zn and the four Zn alloy bilayer films. Generally, as the film’s total thickness increases, \( A \) and \( R \) increases while \( T \) decreases. These three values saturate at a total thickness of around 50nm for all films.
Figure 2-3. RAT curves at a wavelength of 488nm for a single Zn layer

Figure 2-4. RAT curves at a wavelength of 488nm for a bilayer In/Zn (95/5nm) film

Figure 2-5. RAT curves at a wavelength of 488nm for a bilayer In/Zn (25/75nm) film

Figure 2-6. RAT curves at a wavelength of 488nm for a bilayer In/Zn (50/50nm) film
Figure 2-7. \( \text{RAT} \) curves at a wavelength of 488nm for a bilayer Sn/Zn (90/10nm) film

Figure 2-8. \( \text{RAT} \) curves at a wavelength of 488nm for a bilayer Zn/Sn (10/90nm) film

Figure 2-9. \( \text{RAT} \) curves at a wavelength of 488nm for a bilayer Bi/Zn (97/3nm) film

Figure 2-10. \( \text{RAT} \) curves at a wavelength of 488nm for a bilayer Zn/Bi (3/97nm) film

Figure 2-11. \( \text{RAT} \) curves at a wavelength of 488nm for a bilayer Al/Zn (5/95nm) film

Figure 2-12. \( \text{RAT} \) curves at a wavelength of 488nm for a bilayer Zn/Al (95/5nm) film
The absorbed intensity \((A)\) represents the amount of light energy deposited in the film, resulting in a temperature rise. Because this part energy is used for increasing temperature and oxidizing the metals, the value of \(A\) is of the most interest for each film. The \(A\) value of each film for a total film of 100nm thickness is listed in Table 2-5.

Two main points are obtained from this table. Firstly, the absorption varies dramatically (from 10.9% to 56.9%) with film materials. The Bi-Zn bilayer films hold the highest capacity (with absorption values of 49.7~56.9%) to utilize the laser energy. The other Zn alloys will absorb less than 25.7% of the energy at a laser radiation wavelength of 488nm. Secondly, different layer positions of the two metals will result in a difference in the intensity of light absorbed. For example, for Zn-Sn bimetallic film, the absorption when Sn is on top is 131% of that when Zn is on top.

Table 2-5. Absorption intensity of each 100-nm as-deposited film

<table>
<thead>
<tr>
<th>Film</th>
<th>Zn</th>
<th>In/Zn (95/5nm)</th>
<th>In/Zn (75/25nm)</th>
<th>In/Zn (50/50nm)</th>
<th>In/Zn (25/75nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (%)</td>
<td>16.8</td>
<td>15.4</td>
<td>10.9</td>
<td>11.3</td>
<td>12.0</td>
</tr>
<tr>
<td>R (%)</td>
<td>83.1</td>
<td>84.6</td>
<td>89.1</td>
<td>88.7</td>
<td>88.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Film</th>
<th>Al/Zn (5/95nm)</th>
<th>Zn/Al (95/5nm)</th>
<th>Bi/Zn (97/3nm)</th>
<th>Zn/Bi (3/97nm)</th>
<th>Sn/Zn (90/10nm)</th>
<th>Zn/Sn (10/90nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (%)</td>
<td>12.8</td>
<td>16.8</td>
<td>49.7</td>
<td>56.9</td>
<td>25.7</td>
<td>19.9</td>
</tr>
<tr>
<td>R (%)</td>
<td>87.2</td>
<td>83.2</td>
<td>50.3</td>
<td>43.0</td>
<td>74.2</td>
<td>80.0</td>
</tr>
</tbody>
</table>

The optical modelling results show that different materials and film structures affect the film absorption, which in turn influences the total energy deposited in the films for heating and oxidizing, thus varying the OD of the exposed areas.

2.4 Thermal Modelling

Thermal modelling was used to investigate the heat distribution in films and substrates when exposed to laser light radiation. Finite Element Analysis (FEA) software, ANSYS 8.1®, was utilized as the numerical tool in this thermal simulation. ANSYS (ANSYS Inc.) is one of several general-purpose finite element-modelling analysis packages for numerically solving many mechanical situations including static, dynamic, fluid flow and heat transfer problems. In this research, ANSYS 8.1 was used to simulate...
temperature and heat flux distributions in metallic films and glass substrates during laser exposure. To simplify the calculations, the chemical reaction was ignored.

2.4.1 Heat Transfer Model

The thermal model was based on the following simplifying assumptions: (1) the laser spot is a uniform, circular shaped source rather than a more realistic Gaussian distribution; (2) each film and glass substrate are homogeneous and isotropic; (3) the absorption of the film is the value obtained from the optical modelling results in the previous section; (4) the reflectance, re-radiation from the surface and the convection cooling of the surface are ignored; (5) heat generation, phase change, convection and radiation effects are neglected; (6) the optical and thermal characteristics of films are assumed temperature-independent and constant during laser illumination because of the unavailable database.

A thin film on a substrate with laser radiation can be represented as a 3D cylindrical structure (Figure 2-13). Because of its radial symmetry and assuming no angular dependence, this 3D structure can be simplified to a 2D model by using cylindrical polar coordinates.

As shown in Figure 2-14, \( h_{\text{top}} \) is the total thickness of the film, \( h_{\text{bottom}} \) is the thickness of the glass substrate and \( r_0 \) is the radius of the cylindrical film. For this calculation, the film radius, \( r_0 \), is 20\( \mu \)m and the total thickness, \( h \), is 12.1\( \mu \)m with a top thickness (\( h_{\text{top}} \)) of 0.1\( \mu \)m and a bottom thickness (\( h_{\text{bottom}} \)) of 12\( \mu \)m.

The 2D heat flow equation is [86],...
\[ \frac{1}{r} \frac{\partial}{\partial r} \left( k T \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial z} \left( k \frac{\partial T}{\partial z} \right) + \frac{dq}{dt} = \rho c_p \frac{\partial T}{\partial t}, \]

where \( k \) is the thermal conductivity (W/m-K), \( \rho \) is the density (kg/m\(^3\)), \( c_p \) is the specific heat (J/kg-K), \( T \) is temperature (K), \( t \) is time (seconds), and \( q \) is heat flux (W/m\(^2\)), the amount of heat transferring across a unit area surface in a unit time. The boundary and initial conditions are:

**Boundary condition,**

\[ T(z,r) = 298K (z=h)(r=r_o), \]
\[ q = H_s (W/m^2)(z=h, 1 \leq r \leq 5 \mu m) \]

with initial conditions of

\[ T(z,r) = 298K (0 \leq z \leq h, 0 \leq r \leq r_o). \]

\( H_s \) was specified by the laser power and laser spot size shown in equation 2-6. Under a 50mm focal length lens, the laser spot was around 10\( \mu \)m. When the sample moving speed was 1cm/s, the typical exposure time was 1ms. The heat flux can be calculated based on the laser power and spot size using the following equation:

\[ H_s = \frac{4p}{\pi D^2}, \]

where \( p \) is laser power (W) and \( D \) is the diameter (m) of the laser spot.

Because of the absorption and reflection of the lenses and mirrors in the laser path from the laser tube to the film sample, about half of the power is lost in the light path. For example, a 0.4W output laser after passing through three reflection mirrors and one f=50mm lens was measured to be 0.203W by a thermal detector head, LM-30V. In addition, depending on the reflection and absorption property \( (A) \) of the film, only part of laser energy can be absorbed by films. Therefore, the heat flux equation becomes

\[ H_s = \frac{4PA\eta}{\pi D^2}, \]

where \( \eta \) is the ratio (%) of the actual power reaching the sample to the console power value, and \( A \) is the absorption intensity (%).
For this simulation, we chose 100nm Al/Zn and Zn/Al with laser radiation. According to the optical modelling results, 100nm Al/Zn (15/85nm) has a 9.2% absorption ratio while 100nm thick Zn/Al (85/15nm) has a 16.7% absorption ratio. When the laser power used was 0.4W, the heat flux for the Al/Zn and Zn/Al were $2.34 \times 10^8$ W/m² and $4.25 \times 10^8$ W/m², respectively.

### 2.4.2 ANSYS Simulation

A certain physical properties were required for the materials in this simulation. To simplify the calculation, the dependence of the thermal and optical characteristics of the materials during the laser illumination was ignored. The applied material parameters for this ANSYS thermal solid model are summarized in Table 2-6.

<table>
<thead>
<tr>
<th></th>
<th>Thermal conductivity (W/m.K)</th>
<th>Specific heat (J/kg.K)</th>
<th>Density (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>237.00</td>
<td>896</td>
<td>2700</td>
</tr>
<tr>
<td>Zn</td>
<td>116.00</td>
<td>388</td>
<td>7140</td>
</tr>
<tr>
<td>Glass (SiO₂ 75%, soda 17%, and lime 8%)</td>
<td>0.76</td>
<td>800</td>
<td>2707</td>
</tr>
</tbody>
</table>

A manual size control for the rectangle element was applied in the simulation. Depending on the minimum thickness in the film structure and the maximum elements allowed in ANSYS8.1, the available range of element size is very limited. For this simulation, we chose a transient thermal solid model with an axis-harmonic, 4-node, 25 element type.

To explore the calculation dependence on element type and size, two element types (axis-harmonic 4-node and 8-node) as well as three mesh sizes ($9 \times 10^{-7}$ m, $5 \times 10^{-7}$ m and $1 \times 10^{-7}$ m) were used to calculate a 900nm thick single Al film on a glass slide. Shown in Table 2-7, the results show that the highest temperatures calculated with different element models and different edge space sizes were very similar, with a difference less than 0.1%. The consistency in behaviour shows the grids used area sufficiently small to exactly model the thermal process.

The four typical steps run for this simulation were preference, pre-processor, solve and postprocessor. The basic operations are listed in the appendix.
Table 2-7. Comparison of simulation results when different element and size used

<table>
<thead>
<tr>
<th>Element type</th>
<th>Element edge space size(1e-7m)</th>
<th>Highest temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Axi-har 4 node</td>
<td>9</td>
<td>716.306</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>716.264</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>716.234</td>
</tr>
<tr>
<td>Axi-har 8 node</td>
<td>9</td>
<td>716.738</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>716.647</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>716.299</td>
</tr>
</tbody>
</table>

2.4.3 Simulation Results

Figure 2-15 illustrates results for an Al/Zn (15/85nm) film, showing the temperature cross-section distribution of the film and substrate. This thermal distribution was achieved after 1ms of continuous radiation from a 10μm diameter spot of a 0.4W laser power. The values shown in the left corner of the diagram are the transient time, number of steps and substeps, as well as the maximum and minimum temperatures. The top left corner serves as the laser radiation centre, which has the highest temperature, 589.898K. As expected, the temperature decreases away from the laser centre and eventually reaches room temperature.

Figure 2-15. The cross-section temperature distribution simulated by ANSYS 8.1 of a 100nm Al/Zn film illumination with an Argon laser with a heat flux of 2.3E8 W/m² for 1ms
The temperature variation with respect to laser power is shown in Table 2-8. The power values starting from 0.2 with an increasing factor of 2 to 0.8W were applied. The temperature deviation under the same laser power was less than 5%. The Zn/Al binary phase diagram demonstrates that Zn-Al with 85 vol.% Zn is close to the ratio of the eutectic point, 381°C (or 654K), which is between the temperature shown under 0.4W and 0.8W illuminations. Therefore, the thermal distribution of film exposed by a laser with power at 0.6W needs further simulation.

Table 2-8. Simulated results of the highest temperature in Al/Zn and Zn/Al films

<table>
<thead>
<tr>
<th>Laser power(W)</th>
<th>Al/Zn(15/85nm)</th>
<th>Zn/Al(85/15nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>427</td>
<td>439</td>
</tr>
<tr>
<td>0.4</td>
<td>590</td>
<td>581</td>
</tr>
<tr>
<td>0.8</td>
<td>816</td>
<td>864</td>
</tr>
</tbody>
</table>

M. Wautelet [57] [87] reported that a 200nm thick Zn film was fully oxidized at 573K when the film became transparent during a laser illumination process. If the reported number is suitable for our process, we should use the parameters of ZnO instead of Zn at its critical temperature of 573K. A similar consideration is needed for Al, too. However, accurate knowledge on spatial and temporal changes of the optical and thermal material parameters for Zn and Al is not available, so a more exact model cannot be offered currently. Because of the complexity of the practical laser-induced process [74] [81] [82], the accuracy of the simulations cannot be proven, but the calculated results are still helpful for us to compare various bimetallic combinations for the laser writing process.

2.5 Summary

ZnO is a widely-used material, but, to date, no literature shows its application for grayscale photomasks in UV photolithography. This research explored ZnO’s use in this role.

This chapter described the general properties of Zn and ZnO. Because of its wide bandgap (3.2eV at room temperature), pure crystal ZnO highly absorb UV at the I-line wavelength, which limits its potential in UV photolithographic applications. However, the literature reports that changing the ZnO preparation process or adding certain metal
oxides into ZnO can shift the absorption edge of ZnO. A laser-induced partial oxidation process and four metals (Al, Bi, In and Sn) were, therefore, chosen to fabricate Zn alloys. Al oxides, In oxides and Sn oxides were excepted to have better optical characteristics than pure ZnO because of their lower bandgap wavelengths than pure ZnO.

At the end of this chapter, an optical and a thermal model were introduced to estimate the optical and thermal characteristics of films for the laser writing process. The optical model demonstrated that the absorbed intensity of the Zn and Zn alloy film increases while the films became thicker, but they saturate at a total thickness of around 50nm. The ANSYS thermal modelling for 100nm Al/Zn and Zn/Al showed the temperature cross-section distribution within the film and substrate during the laser exposure process.
CHAPTER 3. FABRICATION AND MEASUREMENT OF BIMETALLIC FILMS

3.1 Introduction

Bimetallic thin films have a bilayer structure, whose fabrication starts with a deposition step onto the mask plate. Then laser exposure is used to create the patterns. After the manufacturing procedure, surface investigation and material analysis are carried out for the exposed areas of films. In this chapter, fabrication and measurement processes along with the associated equipments and typical parameters are introduced.

3.2 Deposition Process for Bimetallic Films

The thickness of our pure Zn films varies from 100nm to 240nm whereas all the Zn alloy films investigated have the same total thickness of 100nm. For bimetallic films, each of the two layers has a thickness in the range of 3~97nm, depending on the desired composition for the alloy. The corresponding atomic and thickness ratios of all the alloys are shown in the Table 2-3.

Using a Corona Vacuum Coater sputtering system (shown in Figure 3-1), the two layers in each film were sequentially DC/RF sputtered from two metal targets (Zn and either Al, Bi, Sn or In) onto a transparent substrate.

![Figure 3-1. Picture of Corona Vacuum Coater DC/RF magnetron sputterer](image)
Using the sputter system, by modifying the sputtering rate for each metal, the thickness of each metal as well as the two-layer ratio can be controlled. The most common substrate used in this research was Pearl® (CAT No. 7101) microscope slide (25.4mm×76.2mm×1.2mm), which are around 84.3% transparent at the I-line wavelength (as shown in Figure 1-2).

To remove organic contaminations before film sputtering, the slides were first cleaned with an RCA-1 solution (NH$_4$OH:H$_2$O$_2$:H$_2$O = 1:1:5) at 80°C for 10 minutes [26]. Then, the slides were baked at 120°C for 20 minutes to remove any moisture. During the deposition process, the sputter chamber was pumped down to a low base pressure, around 3~4 mTorr, and argon gas was introduced at around 10 sccm for sputtering. Holding multiple targets, the system deposited multilayer films without breaking the vacuum. The typical sputtering conditions for Zn, Al, Bi, In and Sn thin films are shown in Table 3-1.

<table>
<thead>
<tr>
<th>Material</th>
<th>Deposition Rate (Å/W min)</th>
<th>Sputter Pressure (mTorr)</th>
<th>Sputter Power (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In</td>
<td>4</td>
<td>3.2</td>
<td>101</td>
</tr>
<tr>
<td>Sn</td>
<td>6</td>
<td>3.2</td>
<td>76</td>
</tr>
<tr>
<td>Bi</td>
<td>12</td>
<td>4.0</td>
<td>101</td>
</tr>
<tr>
<td>Al</td>
<td>1</td>
<td>3.0</td>
<td>101</td>
</tr>
<tr>
<td>Zn</td>
<td>4</td>
<td>3.2</td>
<td>95~110</td>
</tr>
</tbody>
</table>

3.3 Laser Exposure Process for Thin Films

Formation of a ZnO layer can be realized by thermal oxidation, sputtering deposition, plasma-assisted oxidation, vacuum evaporation, chemical decomposition, molecular beam epitaxy, spray pyrolysis, laser deposition and laser-assisted oxidation[38][40][42][43][50][56][57][58].

Among these technologies, laser-induced oxidation has gained special attention for its ability to assist localized oxidation with good spatial resolution, a short processing time and its ability to control the thickness of very thin layers at low processing temperatures [70][82]. Of interest to our research, M. Wautelet et al. [56][57] published that the CW argon ion or krypton ion lasers caused Zn films to turn transparent via the oxidation process. However, the literature only discusses the full oxidation of Zn and does not consider the possibility of partial oxidation for grayscale photomasks using Zn.
or Zn alloy thin films. In our research, as-deposited Zn and Zn bimetallic films were partially oxidized by the laser direct-write system, which has been successfully used to oxidize Bi/In and Sn/In thin films [26][27][28].

As shown in Figure 3-2 and Figure 3-3, the laser writing system consists of a CW argon ion laser (488/514nm), a high resolution X-Y-Z table (with a precision of ±0.1µm), an electro-optic shutter, an optical system composed of dielectric mirrors and a lens (f=50mm focus lens or 50× objective lens). The CW argon ion laser, running all lines with a 2.5mm beam diameter, was focused by a lens, either a 50× objective lens or f=50mm lens, to form a laser spot with a diameter of 2 or 10µm, respectively. The whole writing procedure can be real-time monitored by a CCD video camera.

![Figure 3-2. Laser writing system](image)

The process, shown in Figure 3-3, is controlled by the Windows Laser Table Control (WinLTC) program, which allows us to control the movement of the X-Y-Z table to write desired patterns on the thin film with a modulated argon laser [72]. This process involves transferring a computer bitmap to a film grayscale pattern. At first, the designed bitmap pattern (Figure 3-3 (a)) was used for monitoring the electro-optic shutter to control the laser power through the function generator (Figure 3-3 (c)), and, meanwhile, the PictureWriter function in WinLTC manipulated the movement of the X-Y-Z table (Figure 3-3 (b)). The moving velocity adopted in this research was 1cm/s. With this real-time control of the laser power and table moving parameters, an image corresponding to the bitmap were created in the film (Figure 3-3(d)).
A translation matrix is required to simulate the specific voltage for the electro-optic shutter, which in turn corresponds to a specific laser power. To approximate the power range for grayscale writing for each film, a single row of 16 squares (200\(\mu\)m \(\times\) 200\(\mu\)m each) covering the maximum absorption to maximum transmission was created, (see Figure 3-5).

Before a desired grayscale is written in a film, estimating the relationship between OD and laser power is necessary. A 16-square (200\(\mu\)m \(\times\) 200\(\mu\)m each) calibration process and 1cm\(\times\)1cm window cleaning process were used to evaluate the OD response to laser writing power. The 16-square calibration process is highly efficient, but not as accurate as the window cleaning process.
The 16-square pattern was first written at a fixed laser power. Then, a microscope (Olympus BH2-UMA) with a CCD camera (Sony Digital Interface DFW-X700, with XGA square pixel resolution) and a uniform backlit source (NCL 150) were used to inspect and take pictures of the written squares. Figure 3-6 presents a microscope picture of one of the 16 squares (each with a size of 200µm × 200µm) created by the laser at 0.3W with a 50× lens in a In/Zn film.

![Microscope image of a In/Zn laser exposed window area](image)

Figure 3-6. Microscope image of a In/Zn laser exposed window area

The 16-square calibration process is a fast way to determine how each film responds to the laser power [64][68]; however, this test only shows the transmittance in the visible range rather than at the I-line transmission of each film.

A more practical way to test the OD at the I-line of each film is to create windows (each with a size of 1cm × 1cm) using different laser write powers. Writing 10 windows of this size takes 5 hours. The writing process was manipulated by a script or the WTC function named WindowCleaner, in which the parameters are specified (the x dot size, y scanning velocity and sampling frequency). Then, a UV/visible spectrometer (HP8543) was used to measure each window’s transmittance (T %) spectrum, which was converted to an OD value by equation (1-1). Based on the OD value of all the windows, the curve of the OD versus laser power was plotted. For example, Figure 3-7 presents a curve of the OD at the I-line wavelength to laser writing power for a 100nm Sn/Zn film. The film’s OD of 3.7 before exposure changes to 0.26 at 365nm wavelength after 0.4 W of scanning, meaning that transmittance varies from the original 0.02% to 55% after exposure.
3.4 Thin Film Measurements

Both the physical and chemical properties of the exposed metallic films changed after the laser exposure process. The changes of the optical characteristics were measured by a UV/visible spectrometer and an optical microscope for potential mask applications. Material analysis using profilometry, X-Ray Diffractometer (XRD) and Energy-Dispersive X-ray spectrooscope (EDX) were also carried out to better characterize the writing process. This section describes the equipment and the related significant parameters. The next chapter summarizes the related results.

3.4.1 Observation Using the Microscope

The thin film ZnO grown by the laser-induced method is compact with good adherent properties on glass substrates. These oxides are transparent, providing convenient conditions for backlit microscopic investigations. The microscope magnified features of the scanned areas were used to decide which laser power or which film would be further researched. Laser power that created obvious rough textures on certain films are not suggested for fabricating ideal grayscale patterns. Additionally, films that have very rough textures for the most-used laser power range are not considered as materials for improved grayscale photomasks.
A microscope (Olympus BH2-UMA) with a CCD camera (Sony Digital Interface DFW-X700, with XGA square pixel resolution) and a uniform backlit source (NCL 150) were used to inspect and take pictures of the written patterns. Figure 3-8 (left) shows a picture of the Olympus BH2-UMA microscope, and Figure 3-8 (right) presents a pattern in an exposed Zn film, which was scanned with only one laser power, so it presents a binary property after laser exposure. The exposed part, the lighter colour, results from its high transparency to the backlit in the microscope, and the as-deposited part, the black area, blocks the light. Even though this pattern is only binary, it has been used in making microchannels.

Figure 3-8. Picture of an Olympus BH2-UMA microscope (left) and a frame-pattern in a 200nm thick Zn film (right)

The films were inspected with the microscope with 5 to 8 times magnification. Because the light source is in the visible range, the microscope is useful for surface observations and rough transparency comparisons created with different laser powers. This measurement is critical because a clear, smooth and uniform material surface is desired for an ideal photomask.

To study the individuality of each film to laser scanning under the same writing conditions, the single row 16-square pattern (shown in Figure 3-5) was drawn in each Zn and Zn alloy film using an argon ion CW laser (488nm). In the next chapter, the first 200µm × 200µm square of each single row 16-square pattern for each material is shown. In addition, to investigate how the morphological aspects change with laser variation, five
small windows responding to various laser powers were written in each film. The five windows, from left to right, each with a dimension of 140μm × 7000μm, were created using laser power levels of 0.07W, 0.1W, 0.2W, 0.3W and 0.4W through a f=50mm lens with a 7μm line spacing and a 1cm/s write speed.

3.4.2 UV/visible Spectrometer Analysis

For our research, the change in optical properties at the I-line wavelength of each exposed thin film is the most important. We used an HP8453 UV/visible spectrometer to measure the amount of ultraviolet and visible light transmitted or absorbed by the samples. Figure 3-9 (left) is a picture of the spectrometer, and as an example, Figure 3-9 (right) shows a plot of the spectrum for a piece of quartz tested with this spectrometer. From the plot, we can see the transparency of the quartz at different wavelengths.

The HP 8453 UV/visible spectrometer offers many complex features, but the transmittance at 365nm is of interest to us. The spectrum curves in the UV range thus were stored and transferred into Excel files for further analysis.

![Figure 3-9. Picture of an HP 8453 UV/visible spectrometer (left) and its measurement result for a quartz sample (right)](image)

3.4.3 Profilmeter Measurements

The thickness of exposed and unexposed areas was compared to understand the reasons for the OD change of the exposed films. Both laser-induced ablation and oxidation on the metal films can increase the transparency. However, because ablation
occurs at high laser exposures, accurate controlling the OD change in a film is difficult. Profilometry was used to check that oxidation, not ablation, was being used.

A computerized, high-sensitivity surface profilometer, Alpha-Step 500, was used in this research to investigate the roughness and height of films. The profiles can be stored in TIF image file format or ASCII data. The ASCII data can be plotted in EXCEL files. The typical specifications for tests are the following: Scan Length is up to 5000µm, scan speed is 2~200µm/sec, vertical range/resolution is either ±6.5µm/1Å or 300µm/25Å and stylus force is 10mg. Figure 3-10 (top) gives a picture of the Alpha-Step 500 profilometer, and the profile of several microstructures in photoresist patterned by a Zn alloy photomask is shown in Figure 3-10 (bottom). The repeated sine-shape curve presents a few V-groove features with varying heights. The text on the left of the plot shows the corresponding test parameters.

Figure 3-10. Picture of an Alpha-Step 500 profilometer (top) and a measurement example (bottom)
3.4.4 X-Ray Diffraction Analysis

X-ray Diffraction (XRD) is an analytical technique used to identify crystalline solids by measuring the characteristic spaces between the layers of atoms or molecules in a crystal; hence, it generally leads to an understanding of the material composition and the structure of a substance. The XRD analysis was used in the previous research on Bi/In and Sn/In [20][21]. This thesis investigates Zn and Zn alloy bimetallic films using XRD to characterize the films’ composition before and after laser exposure.

In this research, the X-ray diffraction was carried out using a Rigaku R-AXIS RAPID-S diffractometer (shown in Figure 3-11 (top)) equipped with a Cu sealed tube source operating at an extraction voltage of 46 kV and a filament current of 42 mA with a wavelength at 1.540598 Å and 1.544426 Å, respectively. Samples were scanned for 10 minutes ($\omega = 183^\circ$, $\chi = 45^\circ$, $\phi$ spinning at 10°/sec, 300μm collimator). The images obtained were integrated using the AreaMax® software in the range of $10^\circ<\theta<80^\circ$ and $150^\circ<\chi<175^\circ$.

Figure 3-11 (bottom) shows an example of an XRD pattern for a In/Zn (25/75nm) film exposed by different laser densities. The plot not only gives the compositions, but, also by comparing the peak distributions and intensity, the laser density’s effect on the exposed results is shown. More details are provided in chapter 4. Fewer peaks appeared when a smaller spot was used, which suggested that the material was becoming either amorphous or fully aligned at a certain angle.

Two databases were applied to index the XRD peaks by identification of the nearest peaks among Al, Bi, In, Sn, Zn and their oxides. One was the diffraction database PDF-2 (Powder Diffraction Files, sets 1-43, 1993) [65], the other was an inorganic crystal structure database (PHP-MySQL ICSD-for-WWW, 2006) [83].
Figure 3-11. Picture of a Rigaku R-AXIS RAPID-S diffractometer (top) and an XRD patterns of a In/Zn (75/25nm) after exposures with different laser power densities (bottom)

3.4.5 Investigation of Energy-Dispersive X-ray Spectroscopy

Energy-Dispersive X-Ray Spectroscopy (EDX) is a spectroscopy technique for analyzing element distribution of thin films and layered systems. Using the characteristic X-rays, it monitors the electron energy loss through the thin film [66]. An EDX system in Scanning Transmission Electron Microscopy (STEM) was applied in this research for analyzing the elemental concentration of film depth, while EDX in Scanning Electron Microscopy (SEM) was used for investigating the elements of the film’s surface.
Here we used an Al/Zn (15/85nm) film on a silicon wafer as the specimen. Two 1cm×1.5cm windows were scanned through a 50× objective lens with 0.8W and 1.8W lasers, respectively. The two windows, without any additional processing, are used for SEM investigation, unlike the specimen preparation necessary for STEM analysis (details are presented later in this section).

Figure 3-12 gives a picture of the SEM equipment and the measurement results for the 1.8W-exposed window. The cross on the film’s surface shows the area of investigation, where the height of the peaks shows the relative concentration of various elements at this area. In this 1.8W-exposed window, except for Si (the substrate material), the oxide has the strongest concentration among the three possible elements included in the film, which shows that oxidation occurs in the laser scanning process. Compared with the measurement for the 0.8W-exposed window, a higher laser exposure allows for a stronger oxidization (more details are provided in chapter 4).

The EDX in STEM involves investigating the inside of the films, so the sample preparation is complex and time-consuming. The two window areas were separately prepared for the STEM investigation with a one-week process to meet the strict thickness requirement by STEM. Each window was split into two equal parts and then each was glued face to face to form a Si-film-film-Si sandwich structure. The sandwich sample was then cut into small pieces and was polished on the two long edges to ensure they were parallel with a 20μm distance. One of these polished small sandwiches was then glued to a copper grid, which works as a conductive holder in STEM. Finally, to obtain enough electron transparency, the sample was thinned with an argon ion polishing system, in which an etching angle as low as ±10° for the two ion guns and an accelerating voltage of 5kV were applied. A hole was created in the cross-section of the small sandwich by bombarding it with the argon ion laser. The thinnest part, including the open area of film and Si around the hole, was observed by STEM.
Figure 3-12. Picture of the SEM equipment (top) and the test results for the 1.8W-exposed Al/Zn film (bottom)

Figure 3-13 (a) is a picture of the STEM equipment and the cross-section image with 4 numbered circles (Figure 3-13 (b)) represent the positions investigated by the detector using a 0.8W-exposed Al/Zn film. As an example, Figure 3-13 (c) shows the test results for position 3. Oxide still exists in this position, even though it is far away from the surface.
3.5 Summary

The fabrication processes, including the sputtering step and laser scanning step, were introduced in this chapter. After the laser writing step on the deposited films, the OD distribution was available for the subsequent application in UV lithographic process. To investigate the characteristics of each film for application in grayscale photomasks, a set of measurements were obtained using a UV/visible spectrometer, an optical microscope, a profilometer, a XRD and an EDX. The main parameters and mechanism of the individual equipment were introduced in this chapter. This chapter provided the necessary information needed for understanding the coming discussion regarding measurement results.
CHAPTER 4.
MATERIAL CHARACTERISTICS
OF EXPOSED FILMS

4.1 Introduction

Chapter 3 introduced the test methods for material analysis and surface observations on the exposed samples. The typical specifications for each measurement were also listed. This chapter investigates each film with these methods under several laser-scanning conditions.

4.2 Zinc

Zn is a common material used in all the bimetallic films investigated in this research. Before the investigation of these bilayer films, Zn was studied as a single layer film with a thickness of 100nm to 240nm.

4.2.1 Analysis of Microscope Images

A microscope was used to magnify the fine details in the exposed samples. For example, backlit microscope pictures of the laser exposed areas (usually in a rectangular shape) give information on the transparency uniformity of the exposed films to white visible light. Ideally, these squares should show a uniform brightness level. Using Adobe Photoshop software, the mean and standard deviation of grayscale values (0~255) of these laser exposed areas can be measured (0 represents the darkest and 255 represents the brightest). Therefore, the higher value the image has, the brighter, and more transparent it is. However, because of the auto-exposure function of the microscope, the grayscale range of different pictures is not comparable, but the variation within each picture can tell us the extent of uniformity of the observed area. Note that these white light measurements cannot be directly related to the values at 365nm with the UV spectrometer.
Generally, as seen in the microscope observations, the laser exposed Zn films (100–240nm) have a very clear pattern with sharp, straight edges. Figure 4-1 presents three changed areas produced in Zn films, and Table 4-1 lists the grayscale variation and the mean value of each window. Shown in Figure 4-1 (a) and Figure 4-1 (b), the 200µm×200µm squares were created by a one-way raster scanning using a 0.07W power laser with a 2µm diameter spot and 2µm line spacing. Both squares have very smooth and uniform profiles. Relatively, the exposed 100nm thick film (Figure 4-1(a)) displays better film quality (shown in Table 4-1), a smaller grayscale deviation and a higher grayscale value than the 150nm thick film (Figure 4-1 (b)).

![Figure 4-1. The 100nm thick Zn film's backlit microscope pictures of 200µm×200µm windows created with (a) 0.07W laser beam with a 2µm diameter spot and 2µm line spacing in a 100nm thick Zn film, (b) 0.07W laser beam with a 2µm diameter spot and 2µm line spacing in a 150nm thick Zn film and (c) 0.3W laser beam with a 10µm diameter spot and 5µm line spacing](image)

In the same 100nm Zn film, another pattern, shown in Figure 4-1 (c), was generated by a two-way raster scanning using a 0.3W laser beam with a 10µm spot size and 5µm line spacing. The window in Figure 4-1 (c) has lower transparency than the window in Figure 4-1 (a). The Gaussian distribution of the laser spot makes the line edge easily distinguishable, with a 15-level deviation between the line centre and edges even though the Gaussian laser spot of the 0.3W-exposed square had 50% overlap.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>Laser power (W)</th>
<th>Laser spot size (µm)</th>
<th>Grayscale mean</th>
<th>Grayscale deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.07</td>
<td>2</td>
<td>228</td>
<td>3</td>
</tr>
<tr>
<td>150</td>
<td>0.07</td>
<td>2</td>
<td>218</td>
<td>5</td>
</tr>
<tr>
<td>100</td>
<td>0.3</td>
<td>10</td>
<td>215</td>
<td>15</td>
</tr>
</tbody>
</table>

Figure 4-2 shows the reaction of a 200nm thick Zn film to laser exposure when the power was increased from 0.07W to 0.4W with a 10µm spot size and 7µm line spacing. The first three exposed strips showed an increase in transparency, from left to right. The corresponding grayscale values, from left to right, are 37, 201 and 251.
In addition, this microscope image shows a pink colour. This is because the optical characteristics of the ZnO, which is more transparent at the longer wavelengths of the visible light.

Figure 4-2. The 200nm thick Zn film’s backlit microscope picture of five small windows created with various laser exposures (0.07W, 0.1W, 0.2W, 0.3W and 0.4W) with a 10μm diameter spot size

Figure 4-3 provides the relative grayscale value versus the laser writing power. Note that the grayscale level for the last three strips is the same (Table 4-2). Because the camera can only measure less than a 2.4 OD change, we believe the similar brightness was caused from overexposure of the microscope camera; therefore, it could not detect subsequent changes in brightness for the transparent areas. To test this hypothesis, we need to use UV/visible spectrometer to confirm if the film saturates at 0.2W.

Figure 4-3. A 200nm thick Zn film’s grayscale levels of five small windows created with various laser exposures (0.07W, 0.1W, 0.2W, 0.3W and 0.4W) with a 10μm diameter spot size
### Table 4-2. The exposed Zn’s visible light grayscale values

<table>
<thead>
<tr>
<th>Laser power (W)</th>
<th>0.07</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grayscale mean</td>
<td>36</td>
<td>201</td>
<td>251</td>
<td>251</td>
<td>251</td>
</tr>
<tr>
<td>Grayscale deviation</td>
<td>4.1</td>
<td>5.6</td>
<td>0.3</td>
<td>0.4</td>
<td>0.4</td>
</tr>
</tbody>
</table>

#### 4.2.2 UV/visible Spectrometer Analysis

The maximum OD of each film is occupied by the as-deposited area. The solid line in Figure 4-4 illustrates that the OD of the unexposed Zn films changed with thickness. With an increasing film thickness, the maximum OD became larger. This relationship helps in designing a film with a desired maximum OD value. For example, the typical absorbing OD widely used in the semiconductor industry is 3 OD, which, according to Figure 4-4, may be achieved in a 210nm thick Zn film.

![Figure 4-4. Unexposed pure Zn film’s OD versus film thickness](insert)

Based on Beer’s law, this curve should be a straight line with a slope that is the product of a constant and the absorption coefficient. Using a regression linear curve fit (in Excel), shown as a dash line in the figure, we found the absorption coefficient for the Zn films at 365nm wavelength to be 399737/cm. The OD values of the 200nm and 240nm films were deviated from the straight line. This may be caused by the variation of the film density and thickness, resulting from the characteristics of the deposition process.

### Table 4-3. Pure Zn film’s absorption coefficient (1/cm)

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>240</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption coefficient (1/cm)</td>
<td>495055</td>
<td>414465</td>
<td>333874</td>
<td>374170</td>
</tr>
</tbody>
</table>
The most transparent result achieved with Zn was 0.46 OD and was created by a 0.5W (2μm spot size) laser beam in a 200nm Zn film (original OD: 2.8). The resulted absorption coefficient of the exposed area was 52844/cm, which is only 16% of that of the unexposed area.

One of the important parameters of a grayscale mask material is its OD range, which is the difference between the minimum and maximum OD. Figure 4-5 shows that a 240nm thick Zn film with an original OD of 3.74 has a transmittance of 1.26 OD after scanning with a 0.2W (2 spot size). Compared to the 0.2W-exposed area, a 0.4W-exposed area’s OD only decreased an additional 1.05%. This slight OD decrease suggests 0.2W is the saturation power of this film and the OD range for this film is 2.48 OD. Note the transparency of the exposed Zn film is also wavelength-dependent: the film is more transparent to visible light than to the UV light.

![Figure 4-5. The exposed 240nm thick Zn’s transmittance spectrum (maximum OD: 3.9 at 365nm)](image)

A thicker film has a higher maximum OD; however, the minimum OD, created by a sufficient laser exposure, increases with the film thickness. Figure 4-6 shows an example of this phenomenon. We used the UV/visible spectrometer to test the results of 200nm and 240nm thick Zn films exposed with 0-0.4W laser beam. Both films became saturated at 0.2W. The 200nm thick film’s minimum OD is 0.87, which was only 70% of the 240nm thick Zn (1.26 OD).
4.2.3 Profilometry Analysis

After laser exposure, the film surface was changed due to oxidation. This was identified by profilometry of the thickness distributions of the exposed areas.

4.2.3.1 Thickness Versus Laser Power

Figure 4-7 displays the profiles of the five small windows created with 0.07W, 0.1W, 0.2W, 0.3W and 0.4W (10μm spot and 7μm line spacing) in the 200nm Zn film.

Figure 4-7. The 200nm thick Zn film’s profilometry result of the exposed areas created with various laser powers (0.07W, 0.1W, 0.2W, 0.3W and 0.4W) with a 10μm spot size
Table 4-4 shows the estimated thickness and range of these five exposed areas. In the Zn film, higher laser powers cause thicker areas and increased surface roughness. These results suggest the exposed films become thicker because oxygen is absorbed during the laser writing process. XRD analysis, which is introduced in 4.2.4, proves that metal oxides appear in films after laser exposure. Both profilometry and XRD tests demonstrate that the high transparency of the exposed films is not caused by material removal (e.g., laser ablation [84]), but rather by the laser-induced oxidizing process.

<table>
<thead>
<tr>
<th>Laser power (W)</th>
<th>0.07</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (Å)</td>
<td>550</td>
<td>1150</td>
<td>1250</td>
<td>1350</td>
<td>1450</td>
</tr>
<tr>
<td>Thickness range (±Å)</td>
<td>75</td>
<td>850</td>
<td>1050</td>
<td>1425</td>
<td>1780</td>
</tr>
</tbody>
</table>

An important observation worth noting is that extremely high laser powers may cause the exposed areas to become thinner. Figure 4-8 gives a typical example showing this thinning. Three windows in a 200nm thick Zn film (original OD: 2.80) were created by a 0.1W, 0.3W and 0.5W laser beam with a 2μm spot size, respectively. The corresponding peak density is shown in Table 4-5.

<table>
<thead>
<tr>
<th>Laser power (W)</th>
<th>0.1</th>
<th>0.3</th>
<th>0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak density (W/μm²)</td>
<td>0.06</td>
<td>0.19</td>
<td>0.32</td>
</tr>
<tr>
<td>Exposed area’s OD</td>
<td>1.030</td>
<td>0.459</td>
<td>0.463</td>
</tr>
</tbody>
</table>

Figure 4-8 shows the profilometry results of these three windows. Each profile shows an obviously different thickness distribution. The left parts of the graphs are the unexposed areas, with thickness values (Y axis) around zero. The right parts of the graphs are exposed area, with positive or negative thickness values.

Compared to the unexposed area, the 0.06 W/μm²-exposed area (Figure 4-8 (a)), is thicker, implying that additional oxygen was absorbed during laser exposure; however, both the 0.19 W/μm²-exposed area (Figure 4-8 (b)) and 0.32 W/μm²-exposed area (Figure 4-8 (c)) became thinner than their respective as-deposited areas by an average of 50nm and 100nm, respectively. This result suggests that ablation started at these very high power densities.
The XRD analysis (Figure 4-10) demonstrates that the 0.32 W/μm²-exposed area has oxides, which means that this high transparency may result from a combination of the laser ablation and laser oxidation process. M. Wautelet et al. [85] reported a similar result in a laser exposed Sn layer. They assume the thinning was caused by the melted Sn that floated away or the vaporization of tin.

Whether this explanation is suitable for the case shown in Figure 4-8 is difficult to confirm, but we believe that the laser-induced material partial-removal coupled with oxidation is too complex of a process to control. Therefore, it cannot be used for creating grayscale masks. However, one possible application of this particular combined process is producing binary thin film masks. In fact, using this combined process, we created a 0.09 OD area using a 0.3 W laser beam (2μm spot) in a 10/90 nm Cr/Zn film that has a
3.02 OD before exposure. This transparency range (3.02 to 0.09 OD) of a mask is very attractive for ICs and MEMS microfabrication using UV photolithography.

4.2.3.2 Roughness of the Exposed Areas

The profilometry results demonstrate that the laser modified areas became rougher than their original as-deposited areas. This effect is one of the limitations of laser-enhanced metal oxidation [82]. The roughness of the laser scanned areas affects the optical properties and crystallographic texture of the films [56] [69]. In a photolithographic process, a very coarse surface causes heavy scattering and attenuation of the light intensity passing through the photomasks. Additionally, surface defects can be transferred to the photoresist and the layers below, causing undesired height variations in the surface of the 3D structures. For these reasons, patterns with a smooth profile are desired for thin metal film photomasks.

To create a smoother film, we replaced the initial single scanning process with a multi-scan process. Two small windows were drawn using the same maximum laser power. The first window was sequentially scanned using four rates of power at 0.07W, 0.10W, 0.12W and 0.15W with a 10μm spot size. That is, the film was first raster-scanned at 0.07W to create a square opening, followed by a re-scan with the 0.10W, 0.12W and 0.15W. Another window was only scanned using a laser power of 0.15W.

Figure 4-9 and Table 4-6 compare the surface profile of these two exposed windows. Obviously, we can see the repeat scanning (Figure 4-9 (a)) has much lower peaks than those in the singly-scanned area (Figure 4-9 (b)). Table 4-6 gives the roughness values tested by the profilometer in three typical positions (top, middle and bottom) of each exposed window.

The average roughness of the overlapping-scanned area is 435Å compared to 1188Å for the single-scanned area, a reduction of 63%. The overlapped-scanning may gradually oxidize the film, allowing for a more sufficient and even oxidation that generates a smoother surface than the single exposure.
Figure 4-9. Profile comparison of (a) an overlapping-scanned area and (b) a singly-scanned area

Table 4-6. The roughness RA values of the overlapping-scanned and singly-scanned areas

<table>
<thead>
<tr>
<th></th>
<th>Overlapping-scanned area</th>
<th>Singly-scanned area</th>
</tr>
</thead>
<tbody>
<tr>
<td>RA (Å) at the top of the window</td>
<td>470</td>
<td>1203</td>
</tr>
<tr>
<td>RA (Å) at the centre of the window</td>
<td>409</td>
<td>1255</td>
</tr>
<tr>
<td>RA (Å) at the bottom of the window</td>
<td>427</td>
<td>1106</td>
</tr>
<tr>
<td>Average Ra (Å)</td>
<td>435</td>
<td>1188</td>
</tr>
</tbody>
</table>

4.2.4 XRD Analysis

The XRD test characterizes crystalline materials without requiring a complicated sample preparation. As mentioned in Chapter 3, two databases were applied to index the XRD peaks by identification of the nearest peaks among Zn and their oxides. One is the diffraction database PDF-2 (Powder Diffraction Files, sets 1-43, 1993) [65]. Another is a PHP-MySQL lCSD-for-WWW inorganic crystal structure database (2006) [83].

Figure 4-10 shows the composition of the unexposed and scanned area created by a 0.5W laser beam with a 2μm spot size in a Zn film. The profile of this exposed area is shown in Figure 4-8. The XRD pattern shows that after the laser scanning, the pure Zn peaks disappeared and ZnO appeared which confirms the laser direct write involves an oxidation process. According to Table 4-7, because the peak height of the exposed area is less than the original film pattern, the exposure to high power changed the film from a crystalline structure to an amorphous structure.
Table 4-7. The Zn film’s peak height of XRD pattern

<table>
<thead>
<tr>
<th>Curve of as-deposited area</th>
<th>Peak</th>
<th>Zn(002)</th>
<th>Zn(100)</th>
<th>Zn(101)</th>
<th>Zn(102)</th>
<th>Zn(110)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak height</td>
<td>40</td>
<td>39</td>
<td>188</td>
<td>11</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>Standard intensity(%)</td>
<td>53</td>
<td>40</td>
<td>100</td>
<td>28</td>
<td>21</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Curve of exposed area</th>
<th>Peak</th>
<th>ZnO(002)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak height</td>
<td>13</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Standard intensity(%)</td>
<td>44</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

4.3 Zinc & Bismuth Bimetallic Films

Bi has been successfully used to form Bi/In thin films, which has many promising properties for direct-write grayscale photomask and thermal resist applications [21]; therefore, it was included in this research to form Zn alloys. Both Zn/Bi and Bi/Zn films had a total thickness of 100nm, and the thickness ratio of Zn to Bi was 3/97.

4.3.1 Analysis of Microscope Images

Figure 4-11 shows a 200μm×200μm window created by a 0.3W laser beam with a 10μm spot size and 5μm line spacing in a Bi/Zn film. Note the dark dots distributed on the transparent background (white) of the exposed area. After exposure to a laser beam with the same power density, the Bi/Zn has a mean grayscale value as 210 of a deviation of 18, which has a larger standard deviation than the Zn, with a mean value of 215 and a
deviation of 15 (Table 4-1). This unevenness of the exposed Bi/Zn may result from the alloy grain effects.

![Figure 4-11. Backlit microscope pictures of 200μm×200μm windows created with 0.3W laser beam with a 10μm diameter spot in a Bi/Zn film](image)

Figure 4-11 displays the microscope pictures of the changing optical transparency for a range of laser powers from 0.07W to 0.4W of a Zn/Bi film (Figure 4-12 (a)) and a Bi/Zn film (Figure 4-12 (b)). Table 4-8 summarizes the mean value and standard deviation for each visible grayscale film. The corresponding relative grayscale values are shown in Figure 4-13. Note the absolute maximum grayscale of each film is different. Zn/Bi is in a near-linear fashion, but Bi/Zn narrowly changes after 0.1W laser beam scanning and then shows an unusual crest in the curve.

![Figure 4-12. (a) Bi/Zn and (b)Zn/Bi films' backlit microscope pictures of five small windows created with various laser exposures (0.07W, 0.1W, 0.2W, 0.3W and 0.4W) with a 10μm diameter spot size](image)

<table>
<thead>
<tr>
<th>Laser power (W)</th>
<th>Zn/Bi grayscale mean</th>
<th>Bi/Zn grayscale mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.07</td>
<td>229</td>
<td>172</td>
</tr>
<tr>
<td>0.1</td>
<td>245</td>
<td>199</td>
</tr>
<tr>
<td>0.2</td>
<td>240</td>
<td>224</td>
</tr>
<tr>
<td>0.3</td>
<td>241</td>
<td>233</td>
</tr>
<tr>
<td>0.4</td>
<td>248</td>
<td>249</td>
</tr>
</tbody>
</table>

Table 4-8. The exposed Bi/Zn and Zn/Bi’s visible light grayscale values
Figure 4-13. Bi/Zn and Zn/Bi films' camera grayscale levels of five small windows created with various laser exposures (0.07W, 0.1W, 0.2W, 0.3W and 0.4W) with a 10µm diameter spot size.

4.3.2 UV/visible Spectrometer Analysis

The microscope pictures (Figure 4-12) show that both the Bi/Zn and Zn/Bi films became transparent at the start of the laser exposure. A similar result was found in the investigation of the UV/visible spectrometry. Shown in Figure 4-14, both the OD of the Bi/Zn and Zn/Bi dropped significantly at the beginning of the laser scanning.

Figure 4-14. The Bi/Zn and Zn/Bi films' OD response to laser power.

For the Zn/Bi film, after the scanning of a 0.02W laser beam, the OD change achieved 2.5. Then, the film's OD slowly decreased to a minimum OD (1.06 OD) at
0.2W followed by an unexpected increase to 1.24 OD at 0.4W. On the other hand, the Bi/Zn displayed an obviously undesirable response to laser exposure where it fell to a 0.35 OD after a 0.08W exposure and then the OD increased to a peak (0.88 OD) at 0.3W and then decreased to 0.80 OD at 0.4 W. We have never found another OD versus laser power curve that showed this minimum followed by an increased OD value while investigating the Zn alloy films using the same writing process. However, when we repeated this experiment in another Bi/Zn film, we obtained a similar curve.

The reason for this reversing curve is unknown, but we hypothesize that it relates to the optical properties of both metals. As shown in Figure 2-9 and Figure 2-10, more laser power was reflected by the surface of the Zn/Bi film than the Bi/Zn film because the reflectivity of Bi is much lower than Zn (49.7% compared to 83.1% at 488nm). Shown in Table 2-5, 50.3% of laser power is absorbed by Bi/Zn, while only 43.0% is absorbed by Zn/Bi. When the same laser conditions are used, Zn/Bi can only use 85.5% of the laser power Bi/Zn are able to absorb. Thus, as shown in Figure 4-14, Bi/Zn had a larger OD change compared to Zn/Bi (3.6 OD versus 2.7 OD at 0.1 W). As the film became very transparent, more energy was transmitted; however, as the laser power increased, both films became more uniform and have a similar curve trend over 0.3~0.4W power range. This behaviour may demonstrate after a sufficient laser power density scanning, the material compositions and structures of the two exposed films became similar.

4.3.3 Profilometry Analysis

Figure 4-15 presents the profiles of the five small windows created with 0.07W to 0.4W laser beam exposures in the Bi/Zn and Zn/Bi film. The thickness change during each exposed window is shown in Table 4-9. Shown in Table 4-9, both film types displayed a very rough surface of the exposed areas. The Bi/Zn has much higher peaks (up to 1.2μm) than those in the exposed Zn/Bi, in which the highest protuberance is 0.4μm. The average thickness range of the exposed Bi/Zn areas was 287% of that for Zn/Bi films. Among all the investigated films exposed by the same laser scanning conditions (0.07W~0.4W, 10μm spot size and 7μm line spacing), the exposed Bi/Zn shows the coarsest profile.
Figure 4-15. (a) Bi/Zn and (b) Zn/Bi films’ profilometry results of the exposed areas created with various laser powers (0.07W, 0.1W, 0.2W, 0.3W and 0.4W) with a 10μm spot size

Table 4-9. The exposed Bi/Zn and Zn/Bi films’ thickness versus power

<table>
<thead>
<tr>
<th></th>
<th>Laser power (W)</th>
<th>0.07</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi/Zn</td>
<td>thickness (Å)</td>
<td>1350</td>
<td>1275</td>
<td>1625</td>
<td>925</td>
<td>675</td>
</tr>
<tr>
<td></td>
<td>thickness range (±Å)</td>
<td>4075</td>
<td>5500</td>
<td>4210</td>
<td>3350</td>
<td>3075</td>
</tr>
<tr>
<td>Zn/Bi</td>
<td>thickness (Å)</td>
<td>1200</td>
<td>1625</td>
<td>1025</td>
<td>1625</td>
<td>1040</td>
</tr>
<tr>
<td></td>
<td>thickness range (±Å)</td>
<td>1875</td>
<td>1725</td>
<td>1220</td>
<td>1410</td>
<td>1035</td>
</tr>
</tbody>
</table>

4.3.4 XRD Analysis

Figure 4-16 is the XRD pattern of a Zn/Bi film before and after laser exposure. The corresponding values and their standard intensity are shown in Table 4-10. Very interestingly, even before the laser exposure, several oxides were present, such as Bi₂O₃ (111), Bi₁₂ZnO (200) and Bi₁₂ZnO (123), which probably occurred during the film deposition process. Because the laser scanning continued the already started oxidation process, the large OD change occurred at the beginning of the laser exposure (Figure 4-14). Meanwhile, the peak height of Bi₂O₃ of the exposed area is only 1/5 of the as-deposited area, suggesting the film became amorphous.
Figure 4-16. XRD pattern of the Zn/Bi film before and after laser exposure.

Table 4-10. The Zn/Bi film’s XRD peak height and standard intensity

<table>
<thead>
<tr>
<th>Peaks (curve of as-deposited area)</th>
<th>Bi$<em>2$ZnO$</em>{20}$ (200)</th>
<th>Bi (003)</th>
<th>Bi$_2$O$_3$ (111)</th>
<th>Bi$_2$ZnO (123)</th>
<th>Bi (110)</th>
<th>Bi (015)</th>
<th>Bi (113)</th>
<th>Bi (202)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak height</td>
<td>22</td>
<td>61</td>
<td>480</td>
<td>199</td>
<td>22</td>
<td>12</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>Standard intensity (%) [65] [83]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peaks (curve of as-deposited area)</td>
<td>Bi (024)</td>
<td>Bi (107)</td>
<td>Bi (116)</td>
<td>Bi (018)</td>
<td>Bi (214)</td>
<td>Bi (027)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak height</td>
<td>9</td>
<td>7</td>
<td>17</td>
<td>7</td>
<td>7</td>
<td>8</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>Standard intensity (%) [65] [83]</td>
<td>9</td>
<td>6</td>
<td>13</td>
<td>16</td>
<td>11</td>
<td>2</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>Peak (curve of exposed area)</td>
<td>Bi$_2$O$_3$ (111)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>Peak height</td>
<td>94</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>Standard intensity (%) [65] [83]</td>
<td>100</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td></td>
</tr>
</tbody>
</table>

4.4 Zinc & Indium Bimetallic Films

In/Zn films were chosen for investigating the composition ratio:

- 95/5—the closed eutectic ratio
- 75/25—Zn oxide with In doping
- 50/50—half Zn and half In
- 25/75—In oxide with Zn doping

all had the same thickness of 100nm and the same layer structure, with the In layer on top and the Zn on the bottom.
4.4.1 Analysis of Microscope Images

The microscope observations compare the optical transparency of the exposed films to visible light. As shown in Figure 4-17 and Figure 4-18, 200μm×200μm windows were created in a 25/75nm and a 95/5nm In/Zn film.

![Figure 4-17. (a) 25/75nm and (b) 95/5nm In/Zn films' backlit microscope pictures of 200×200μm² windows created by 0.07W argon ion CW laser with a 2μm diameter spot](image)

The changed areas shown in Figure 4-17 were produced with a 0.07W laser beam (2μm spot size and 2μm line spacing), and the ones shown in Figure 4-18 were generated with a 0.3W laser beam (10μm diameter spot and 5μm line spacing). Table 4-11 shows that the exposed 95/5nm In/Zn film (Figure 4-17 (b)) displays more uniformity than the 25/75nm In/Zn film (Figure 4-17 (a)). As shown in their grayscale variation after the 0.3W exposure, the laser exposed areas in these two films (Figure 4-18 (a) and (b)) are also different. This difference suggests that when designing a bimetallic film to achieve a desired transparency, the ratio of the two metals needs to be considered.

![Figure 4-18. (a) 25/75nm and (b) 95/5nm In/Zn films' backlit microscope pictures of 200×200μm² windows created by a 0.3W argon ion CW laser beam with a 10μm diameter spot](image)

<table>
<thead>
<tr>
<th>In/Zn thickness ratio</th>
<th>Laser power (W)</th>
<th>Spot size (μm)</th>
<th>Grayscale mean</th>
<th>Grayscale deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>25/75</td>
<td>0.07</td>
<td>2</td>
<td>175</td>
<td>9</td>
</tr>
<tr>
<td>95/5</td>
<td>0.07</td>
<td>2</td>
<td>213</td>
<td>5</td>
</tr>
<tr>
<td>25/75</td>
<td>0.3</td>
<td>10</td>
<td>221</td>
<td>6</td>
</tr>
<tr>
<td>95/5</td>
<td>0.3</td>
<td>10</td>
<td>204</td>
<td>11</td>
</tr>
</tbody>
</table>
Figure 4-19 gives the backlit microscope pictures of three In/Zn films. The visible transparency of the first three strips of the 95/5nm (Figure 4-19 (a)) and 25/75nm film (Figure 4-19 (b)) showed an increasing trend from left to right; however, the 50/50nm film (Figure 4-19 (c)) showed a jump in transparency from the 0.1W-exposed and 0.2W-exposed area. Meantime, we can see, as shown in Table 4-12, the grayscale level of the 0.2~0.4W-exposed areas of the 95/5nm and 50/50nm In/Zn was around 255 and the deviation was 0 or near to 0; therefore, these two pictures of the 95/5nm film were believed to be overexposed by the camera. Therefore, using these pictures, we cannot compare the evenness of these exposed areas.

![Figure 4-19](image)

Figure 4-19. (a) 95/5nm, (b) 25/75nm and (c) 50/50nm In/Zn films' backlit microscope pictures of five small windows created with various laser exposures (0.07W, 0.1W, 0.2W, 0.3W and 0.4W) with a 10μm diameter spot size

<table>
<thead>
<tr>
<th>Table 4-12. The exposed In/Zn films' visible light grayscale values</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Laser power (W)</strong></td>
</tr>
<tr>
<td>In/Zn (95/5nm)</td>
</tr>
<tr>
<td>grayscale mean</td>
</tr>
<tr>
<td>grayscale deviation</td>
</tr>
<tr>
<td>In/Zn (25/75nm)</td>
</tr>
<tr>
<td>grayscale mean</td>
</tr>
<tr>
<td>grayscale deviation</td>
</tr>
<tr>
<td>In/Zn (50/50nm)</td>
</tr>
<tr>
<td>grayscale mean</td>
</tr>
<tr>
<td>grayscale deviation</td>
</tr>
</tbody>
</table>

Shown in Figure 4-20, compared to the 50/50nm, after exposure to a 0.2W laser beam, the change in the camera grayscale level for the 95/5nm and 25/75nm was smaller. Therefore, to cause the same transparency change in all three films, less laser power is required for the 50/50nm film.
4.4.2 UV/visible Spectrometer Analysis

Figure 4-21 gives the OD spectra of the In/Zn (95/5nm) film exposed by lasers with different laser power densities.

As a Gaussian distribution, the peak laser density of a 2µm diameter spot is 25 times greater than 10µm diameter spot. For example, for a 0.5W laser beam, the peak
power density is 0.013 W/μm² when the spot diameter is 10μm and 0.318 W/μm² when it is 2μm. As shown in Figure 4-21, the area scanned by the 0.5W laser beam with a 2μm spot had a 0.23 OD at the I-line wavelength, which was only 19.4% of the OD of the area exposed by the 0.5W laser beam with a 10μm spot. This result showed that the 10μm spot does not have the power density to reach full transparency in this material.

Using a sufficient laser power with a peak density of 0.510W/μm² (0.8W with a 2μm diameter spot), a very transparent film was created in an In/Zn (25/75nm) film. Its transmittance spectrum is shown in Figure 4-22. This 25/75nm In/Zn film had a 3.20 OD in the as-deposited area and a 0.20 OD at the exposed part, achieving a 3 OD range at the I-line wavelength. This OD range is over double of that reported in HEBS glass [16].

![Transmittance Spectrum](image)

**Figure 4-22.** The exposed 25/75nm In/Zn transmittance spectrum (maximum OD: 3.2 at 365nm)

Figure 4-23 presents the In/Zn films’ OD dependence on laser exposure. The OD range of the 95/5nm film was around 2, but its maximum transparency was only around 11.1% (0.95 OD), which is too low for practical mask applications. Although the maximum transparency for the 75/25nm is better, at 26% (0.58 OD), the change in OD for this film is too narrow, only 1.1 OD. The 50/50nm film had a 2.3 OD range, the maximum change obtained among these four In/Zn films; however, its maximum transparency of 34% with an OD of 0.46 was less than the 25/75nm film that had the highest transparency, 48% (0.32 OD). Clearly, each film has its drawbacks, resulting in no clear In/Zn candidate for grayscale mask materials.
4.4.3 Profilometry Analysis

In the exposed 95/5nm film (Figure 4-24 (a)), the height of the scanned pillars keeps increasing until 0.2W and then slightly decreases at 0.4W. For the 50/50nm film (Figure 4-24 (b)), the height of the scanned areas keeps increasing during the whole laser range from 0 to 0.4W. A similar trend is shown in (Figure 4-23). This result is reasonable because the higher transparency results from more oxides forming in the exposed area, creating the higher heights of these parts with a lower OD.

Figure 4-23. OD response to laser power of In/Zn film with different ratios

Figure 4-24. (a) 95/5nm and (b) 50/50nm In/Zn films’ profilometry results for the exposed areas created with various laser powers from 0.07W to 0.4W with a 10μm diameter spot size
Table 4-13 shows the roughness distribution of the exposed areas in the two In/Zn films (Figure 4-24). After exposure by the same laser, the thickness of the 95/5nm film showed a much smaller deviation compared to Bi/Zn and Zn/Bi (Table 4-9), suggesting the exposed In/Zn had a smoother surface.

Table 4-13. The exposed In/Zn films' thickness versus power

<table>
<thead>
<tr>
<th>Laser power (W)</th>
<th>0.07</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>95/5nm In/Zn</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>thickness</td>
<td>1200</td>
<td>2750</td>
<td>2950</td>
<td>3000</td>
<td>2920</td>
</tr>
<tr>
<td>thickness range (Å)</td>
<td>150</td>
<td>610</td>
<td>600</td>
<td>1025</td>
<td>950</td>
</tr>
<tr>
<td>50/50nm In/Zn</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>thickness</td>
<td>50</td>
<td>150</td>
<td>1225</td>
<td>1400</td>
<td>2300</td>
</tr>
<tr>
<td>thickness range (Å)</td>
<td>350</td>
<td>1130</td>
<td>2165</td>
<td>2310</td>
<td>900</td>
</tr>
</tbody>
</table>

4.4.4 XRD Analysis

Figure 4-25 presents the XRD patterns of an as-deposited area and a 0.07W-exposed area in the 25/75nm In/Zn film. The peak height and corresponding standard values are shown in Table 4-14.

Except for the pure metals (indium and zinc), the oxides (ZnO and Zn$_3$In$_2$O$_6$) with very weak intensity also show in the as-deposited area. After laser scanning, the pure metal peaks disappeared and more oxide peaks appeared; however, the peaks are not as high as the ones in the as-deposited film, which implies that the structure is starting to become amorphous.
Table 4-14. The 25/75nm In/Zn film’s XRD peak height

<table>
<thead>
<tr>
<th>Curve of as-deposited area</th>
<th>Peak</th>
<th>In (101)</th>
<th>ZnO (101)</th>
<th>Zn (100)</th>
<th>Zn$_3$InO$_6$ (110)</th>
<th>ZnO (103)</th>
<th>In (211)</th>
<th>Zn (110)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak height</td>
<td></td>
<td>454</td>
<td>138</td>
<td>43</td>
<td>27</td>
<td>9</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>Standard intensity (%)</td>
<td></td>
<td>65</td>
<td>83</td>
<td>100</td>
<td>40</td>
<td>67</td>
<td>29</td>
<td>23</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Curve of exposed area</th>
<th>Peak</th>
<th>In$_2$O$_3$ (222)</th>
<th>(ZnO)$_2$In$_2$O$_3$ (0111)</th>
<th>In$_2$O$_3$ (440)</th>
<th>ZnO (103)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak height</td>
<td></td>
<td>123</td>
<td>11</td>
<td>27</td>
<td>5</td>
</tr>
<tr>
<td>Standard intensity (%)</td>
<td></td>
<td>65</td>
<td>83</td>
<td>100</td>
<td>40</td>
</tr>
</tbody>
</table>

Figure 4-26 displays the XRD patterns of an In/Zn film exposed by a laser with a different laser power density. The corresponding peak heights and standard intensities are shown in Table 4-15.

Figure 4-26. XRD patterns of In/Zn (75/25nm) before and after laser exposure with different power densities

For the as-deposited In/Zn film, both metal and oxides were found in the bottom curve. After a laser exposure of 0.3W using the 50 mm lens, which created a 10μm diameter spot (laser peak density: 0.008W/μm$^2$), some new oxides appeared. Then after another exposure with the same power focused by the 50× objective lens for a 2μm
diameter spot (laser peak density: 0.191W/μm²), most peaks disappeared and only one oxide peak was left. Fewer peaks appeared when the laser power density increased, suggesting that the material was becoming either amorphous or fully aligned at one angle.

<table>
<thead>
<tr>
<th>Curve of as-deposited area</th>
<th>Peak</th>
<th>In₂O₃ (110)</th>
<th>ZnO (101)</th>
<th>Zn (100)</th>
<th>Zn₁InO₆ (110)</th>
<th>ZnO (103)</th>
<th>In (211)</th>
<th>Zn (110)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak height</td>
<td>92</td>
<td>13</td>
<td>9</td>
<td>6</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>—</td>
</tr>
<tr>
<td>Standard intensity (%)</td>
<td>95</td>
<td>100</td>
<td>40</td>
<td>67</td>
<td>29</td>
<td>23</td>
<td>100</td>
<td>—</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Curve of 0.3W (10μm spot) exposed area</th>
<th>Peak</th>
<th>In₂O₃ (011)</th>
<th>In₂O₃ (110)</th>
<th>ZnO₂In₂O₃ (0111)</th>
<th>In₂O₃ (440)</th>
<th>Zn₂In₂O₆ (110)</th>
<th>ZnO (110)</th>
<th>ZnO (103)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak height</td>
<td>11</td>
<td>40</td>
<td>8</td>
<td>8</td>
<td>3</td>
<td>9</td>
<td>5</td>
<td>—</td>
</tr>
<tr>
<td>Standard intensity (%)</td>
<td>20</td>
<td>100</td>
<td>95</td>
<td>100</td>
<td>37</td>
<td>67</td>
<td>100</td>
<td>29</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Curve of 0.3W (2μm spot) exposed area</th>
<th>Peak</th>
<th>In₂O₃ (110)</th>
<th>—</th>
<th>—</th>
<th>—</th>
<th>—</th>
<th>—</th>
<th>—</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak height</td>
<td>8</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Standard intensity (%)</td>
<td>95</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

### 4.5 Zinc & Aluminium Bimetallic Films

Among the four metals (Al, Bi, In and Sn) used with Zn to form Zn alloys, Al has the highest melting point, thermal conductivity, and reflectivity, thus requiring a high laser power scanning before the melting of the alloy which appears to be linked to rapid oxidation of the film. The energy bandgap of Al oxide (8eV) [47] [48] is much greater than that of the oxides of In (3.6eV) [45] [46], Bi (2.7eV) [51] and Sn (3.4–4.6eV) [44]. This difference may allow the exposed Zn and Al bimetallic films to be more transparent at the I-line or below than the other exposed Zn alloys.

In addition, to analysis by a microscope, UV/visible spectrometer, profilometry and XRD, we also used Energy-Dispersive X-ray (EDX) spectroscopy, to investigate this particular Zn alloy combination. We explored films of Zn/Al and Al/Zn with a total thickness of 100nm and the Al to Zn ratio was 5/95.
4.5.1 Analysis of Microscope Images

Figure 4-27 shows the backlit pictures of the exposed Zn/Al and Al/Zn.

![Figure 4-27. (a) Zn/Al and (b) Al/Zn films' backlit microscope pictures of 200 x 200\(\mu m^2\) windows created by 0.07W argon ion CW laser beam with a 2\(\mu m\) diameter spot]

From the microscope observations on the Zn/Al and Al/Zn films, the profile of the exposed area was influenced by the sequence of the layers. Comparing Figure 4-27 (a) and Figure 4-27 (b), both Al/Zn and Zn/Al had limited Al (5%), but the transparency and uniformity of the exposed Zn/Al film was quite different compared to the exposed Al/Zn by the same laser power of 0.07 W with a spot size as 2\(\mu m\) (laser power peak intensity: 0.044\(W/\mu m^2\)). In addition, the Zn/Al film showed large uneven areas whose cause is not understood. The Zn/Al film with Zn on the top gave some large transparent dots in the opaque background, while Al/Zn with Al on the top was more transparent with even features.

These observations may relate to the difference between reflectivity (83% for Zn and 92% for Al) and their thermal conductivity (1.16\(W/cm.K\) for Zn and 2.37\(W/cm.K\) for Al). When aluminium was the top layer, less laser energy was absorbed and the heat spread more rapidly across the film, compared to film with zinc on top. Therefore, this heating may mean that the exposed Al/Zn film had a more even pattern than the exposed Zn/Al film.

In the same Zn/Al film, using a laser power of only 0.3W with a 10\(\mu m\) spot size (the laser peak intensity: 0.008\(W/\mu m^2\)), we created another window (Figure 4-28). Shown in Table 4-16, the grayscale deviation of these two windows in the Zn/Al film is the same after two exposures with different power densities. However, the mean grayscale value of areas, exposed by a laser with a peak intensity of 0.008 \(W/\mu m^2\), is nearly double of the value compared to exposure by a 0.044 \(W/\mu m^2\) laser. These results demonstrate that creating an ideal smooth (low grayscale deviation) and transparent (high grayscale levels) profile requires a suitable laser power range.
Table 4-16. The visible light grayscale values of the exposed Zn/Al and Al/Zn

<table>
<thead>
<tr>
<th>Film</th>
<th>Laser power (W)</th>
<th>spot diameter (µm)</th>
<th>Grayscale mean</th>
<th>Grayscale deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn/Al</td>
<td>0.07</td>
<td>2</td>
<td>98</td>
<td>33</td>
</tr>
<tr>
<td>Al/Zn</td>
<td>0.07</td>
<td>2</td>
<td>179</td>
<td>19</td>
</tr>
<tr>
<td>Zn/Al</td>
<td>0.3</td>
<td>10</td>
<td>183</td>
<td>33</td>
</tr>
</tbody>
</table>

Figure 4-28. Zn/Al film’s backlit microscope pictures of 200×200µm² window created by a 0.3W argon ion CW laser beam with a 10µm diameter spot

Figure 4-29 presents the transparency of the 5 small windows created by scanning with various powers from 0.07~0.4W. Using Photoshop’s Histogram function, we found the grayscale mean and deviation of each strip (Table 4-17). The relative mean values (%) are plotted in Figure 4-30. Obviously, Zn/Al had a larger visible light transparency change while Al/Zn displayed a more gradually increasing rate of transparency.

Table 4-17. The exposed Zn/Al and Al/Zn films’ visible light grayscale values

<table>
<thead>
<tr>
<th>Laser power (W)</th>
<th>0.07</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn/Al Grayscale mean</td>
<td>121</td>
<td>133</td>
<td>235</td>
<td>240</td>
<td>241</td>
</tr>
<tr>
<td>Grayscale deviation</td>
<td>7</td>
<td>7</td>
<td>4</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Al/Zn Grayscale mean</td>
<td>164</td>
<td>194</td>
<td>226</td>
<td>234</td>
<td>240</td>
</tr>
<tr>
<td>Grayscale deviation</td>
<td>13</td>
<td>17</td>
<td>11</td>
<td>7</td>
<td>2</td>
</tr>
</tbody>
</table>
4.5.2 UV/visible Spectrometer Analysis

Figure 4-31 shows the OD versus laser power curves for Zn/Al and Al/Zn. In the 0.07–0.2W power range, Al/Zn presents a nearly linear OD response to laser power. On the other hand, for Zn/Al film, a rise in OD at the centre makes creating patterns with controllable grayscales difficult in the 0.1–0.15W range. However, both films had a large usable power range of over 0.3W with over a 2 OD change, which was better than both Bi and In Zn alloy bimetallic films.
4.5.3 Profilometry Analysis

The profilometry study for Zn/Al and Al/Zn films are shown in Table 4-18 and Figure 4-32. The average roughness value for Zn/Al is 124% of the Al/Zn value, which corresponded to a higher roughness; however, the thickness of the scanned Zn/Al areas showed a slight growing trend with increasing power, suggesting it has a higher sensitivity to thickness with laser scanning than Al/Zn.

<table>
<thead>
<tr>
<th>Laser power (W)</th>
<th>0.07</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn/Al Thickness (Å)</td>
<td>550</td>
<td>450</td>
<td>725</td>
<td>1050</td>
<td>1350</td>
</tr>
<tr>
<td>Thickness range (=Å)</td>
<td>1200</td>
<td>1825</td>
<td>1300</td>
<td>2625</td>
<td>575</td>
</tr>
<tr>
<td>Al/Zn Thickness (Å)</td>
<td>800</td>
<td>900</td>
<td>725</td>
<td>650</td>
<td>625</td>
</tr>
<tr>
<td>Thickness range (=Å)</td>
<td>1375</td>
<td>2300</td>
<td>2325</td>
<td>2400</td>
<td>2525</td>
</tr>
</tbody>
</table>

Figure 4-32. (a) Zn/Al and (b) Al/Zn films’ profilometry results of the 5 small windows

4.5.4 XRD Analysis

Table 4-19 and Figure 4-33 introduces the XRD pattern of a Zn/Al film before and after exposure using a 1W laser beam with a 2μm spot size. Table 4-19 gives the peak heights and the corresponding standard intensity (%). This film’s OD changed from 3.08 to 0.25 after laser scanning, achieving the most transparency among all the Zn and Al bimetallic films.
Table 4-19. The Zn/Al film’s XRD peak height

<table>
<thead>
<tr>
<th>Curve of as-deposited area</th>
<th>Peak</th>
<th>Zn (111)</th>
<th>Al$<em>{0.71}$Zn$</em>{0.29}$ (101)</th>
<th>Zn (100)</th>
<th>Al (200)</th>
<th>ZnO (201)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peak height</td>
<td>21</td>
<td>13</td>
<td>64</td>
<td>3</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Standard intensity (%)</td>
<td>60</td>
<td>100</td>
<td>40</td>
<td>100</td>
<td>11</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Curve of exposed area</th>
<th>Peak</th>
<th>ZnAl$<em>{10}$O$</em>{4}$ (200)</th>
<th>ZnO (100)</th>
<th>—</th>
<th>—</th>
<th>—</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peak height</td>
<td>45</td>
<td>29</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>Standard intensity (%)</td>
<td>23</td>
<td>40</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

As shown in Figure 4-33, after an exposure with very high peak intensity (0.5W/µm$^2$), the Zn and Al peaks disappeared and a Zn and Al compound oxide was formed in the exposed area. Obviously, compared to the pattern of the as-deposited area, fewer peaks appear in the pattern of the exposed area, suggesting the film became amorphous after this exposure with a sufficient laser power density.

4.5.5 Energy-Dispersive X-Ray (EDX) Spectroscopy

In this research, an EDX Spectroscope was also used to explore the element distribution in both the film surface (using EDX in a SEM machine) and inside of the film (using EDX in a STEM machine). Particularly, the oxygen distribution inside of the film indicates the depth of the oxidizing process through the bimetallic film.
Using a 0.8W and 1.8W laser beam power with a 2µm spot size, several windows were created in an Al/Zn (15/85nm) film on a silicon wafer and then they were investigated with both a SEM and STEM. We used silicon as a substrate rather than glass because identifying oxygen in the films is easier. Moreover, silicon's higher thermal conductivity allows us to use a higher laser power for conversion.

4.5.5.1 STEM EDX Analysis

As introduced in chapter 3, the sample preparation for EDX in a STEM is very time-consuming, but this complicated process can lead to a further understanding of the laser-induced oxidation within the film rather than just on the surface. The EDX results qualitatively demonstrate the extent of oxidation within the cross-section of the film by comparing the amount (peak height) of each element present.

Shown in Figure 4-34, Figure 4-35 and Figure 4-36, the top photo in each figure displays the cross-section of the sample: Si (gray), Al/Zn film (white) and vacuum (black). In the top picture of each figure, four circles with numbered markers from 1 to 4 represent the measured positions with decreasing depth within the film. Therefore, number 4 represents the closest position to the open surface and 1 represents the nearest position to the Si wafer substrate. The four plots under the cross-section picture, with the element energy (eV) as the x-axis and the count amount as the y-axis, show the relative distribution of the amount of each element from position 1 (left, second row) to position 4 (right, third row) with reducing depth. Therefore, the Si concentration decreased from point 1 to point 4, shown in Figure 4-34, Figure 4-35 and Figure 4-36.

Figure 4-34 displays the distribution of the amount of each element within an unexposed Al/Zn film. The Zn amount is similar from points 1 to 3, but it dramatically drops down at point 4 (which is at the interference of air and film). Al, on the other hand, with a relatively low percentage (15%) in the bimetallic film, shows no obvious variation through the whole film.
Figure 4-34. STEM EDX results for the as-deposited Al/Zn film

Figure 4-35 and Figure 4-36 show the oxidizing extent within the films after exposure to different levels of laser power. We determined that two points were out of the film: point 4, which was caused by interference of the vacuum and film in the as-deposited film (Figure 4-34); and point 1, in the Si substrate of the 0.8W-exposed area (Figure 4-35). For each area, in order to compare the amount for each point, which is within the film, we estimated the peak heights and then calculated their ratios and corresponding errors.

Table 4-20 shows the element ratios of Al/Zn and O/Zn. Note, the ratios in the table surrounded with double line borders are for two special points, where the data is for either the substrate or the film surface. Because of this ambiguity, these points are not included in below discussion below.
Figure 4-35. STEM EDX results for a 0.8W-exposed area of Al/Zn film with a Si substrate

The Al/Zn ratio of the as-deposited film was measured to be between 0.17~0.21, which was over three times of the expected error and was close to the film’s original thickness ratio of 15/85, about 0.18. For the O/Zn ratios, only the 1.8W-exposed area is non-zero, which may suggest that the 1.8W-exposed area had a stronger oxidation than the 0.8W-exposed area.

Table 4-20. Element ratios of the Al/Zn film

<table>
<thead>
<tr>
<th>Point</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al/Zn</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As-deposited</td>
<td>0.20±0.06</td>
<td>0.17±0.04</td>
<td>0.21±0.05</td>
<td>0.50±0.40</td>
</tr>
<tr>
<td>0.8W-exposed</td>
<td>N/A</td>
<td>0.40±0.29</td>
<td>0.13±0.05</td>
<td>0.21±0.05</td>
</tr>
<tr>
<td>1.8W-exposed</td>
<td>0.50±0.40</td>
<td>0.17±0.10</td>
<td>0.20±0.12</td>
<td>0.17±0.10</td>
</tr>
<tr>
<td>O/Zn</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As-deposited</td>
<td>0.00±0.05</td>
<td>0.00±0.03</td>
<td>0.00±0.04</td>
<td>0.00±0.27</td>
</tr>
<tr>
<td>0.8W-exposed</td>
<td>N/A</td>
<td>0.00±0.21</td>
<td>0.00±0.04</td>
<td>0.00±0.04</td>
</tr>
<tr>
<td>1.8W-exposed</td>
<td>0.05±0.28</td>
<td>0.03±0.09</td>
<td>0.04±0.10</td>
<td>0.03±0.09</td>
</tr>
</tbody>
</table>
Table 4-21 compares the difference between the element ratios of the as-deposited area, the 0.8W-exposed area and the 1.8W-exposed area. A negative number indicates that the ratio of the first area is smaller than that of the second area listed in the table. Both of the differences of the Al/Zn and O/Zn are within the corresponding expected error, and thus the change of element ratio may not be significant.

Figure 4-36. STEM EDX results for a 1.8W-exposed area in an Al/Zn film with a Si substrate
Table 4-21. Difference of element ratios of the Al/Zn film

<table>
<thead>
<tr>
<th>Point</th>
<th>As-deposited area and 0.8W-exposed area</th>
<th>0.8W-exposed area and 1.8W-exposed area</th>
<th>0.8W-exposed area and 1.8W-exposed area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al/Zn difference</td>
<td>-0.23±0.33</td>
<td>-0.08±0.10</td>
<td>-0.23±0.30</td>
</tr>
<tr>
<td>O/Zn difference</td>
<td>0.23±0.39</td>
<td>0.07±0.17</td>
<td>-0.04±0.14</td>
</tr>
</tbody>
</table>

4.5.5.2 SEM EDX Analysis

EDX in SEM was used to compare the surface element distribution between the 0.8W-exposed window (Figure 4-37) and the 1.8W-exposed window (Figure 4-38). The cross in the top picture of each figure represents the investigated position in the film surface. The bottom plot of each figure displays the elemental concentration at the cross point. Figure 4-37 shows that the amount of Zn in the 0.8W-scanned area is much greater than oxygen and Al. However, for the 1.8W-scanned area (Figure 4-38), oxygen occupied the strongest intensity. This difference demonstrates that stronger oxidation took place in the area exposed by a laser with higher power.

Table 4-22 estimates the count ratios of Al/Zn and O/Zn on the 0.8W-exposed and 1.8W-exposed surfaces. The changes of the surface are more prevalent than the changes within the film (Table 4-20). Table 4-23 summarizes the ratio difference of these two exposed areas. A negative number indicates that the ratio of the 0.8W-exposed area is smaller than that of the 1.8W-exposed area. The difference for the Al/Zn and O/Zn, when compared to the expected error, was two and eight times greater, respectively. This result indicates that the change of elements was significant, especially for oxygen. Thus, the vaporization of Zn and Al may happen at the film’s surface. More importantly, a stronger oxidation occurred during a higher power scanning process.

Combining the element comparisons for STEM and SEM EDX results, we found that the 1.8W-exposed area offered a stronger and deeper oxidation than the 0.8W-exposed area, which suggests that a full range oxidation within a film requires a laser exposure with sufficient power. A higher laser power, as long as it is under the saturation value, can make film oxidation stronger.
Figure 4-37. SEM EDX result for a 0.8W-exposed area in Al/Zn film with a Si substrate
Figure 4-38. SEM EDX result for a 1.8W-exposed area in Al/Zn film with a Si substrate

Table 4-22. Element ratios of the 0.8W-exposed and 1.8W-exposed Al/Zn surface

<table>
<thead>
<tr>
<th></th>
<th>0.8W-exposed area</th>
<th>1.8W-exposed area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al/Zn</td>
<td>0.10±0.05</td>
<td>0.43±0.10</td>
</tr>
<tr>
<td>O/Zn</td>
<td>0.10±0.05</td>
<td>2.71±0.27</td>
</tr>
</tbody>
</table>
Table 4-23. Element ratio difference of the 0.8W-exposed and 1.8W-exposed Al/Zn surface

<table>
<thead>
<tr>
<th></th>
<th>Difference of 0.8W-exposed and 1.8W-exposed area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al/Zn</td>
<td>-0.33±0.15</td>
</tr>
<tr>
<td>O/Zn</td>
<td>-2.61±0.32</td>
</tr>
</tbody>
</table>

4.6 Zinc & Tin Bimetallic Films

Both Zn/Sn and Sn/Zn with a total thickness of 100nm were explored in this research. The thickness ratio of Zn to Sn was 10/90.

4.6.1 Analysis of Microscope Images

Among all the 200μm × 200μm windows created by a 0.3W laser beam with a 10μm spot size in the Zn alloy films (Figure 4-11, Figure 4-18 and Figure 4-28), the exposed Sn/Zn (Figure 4-39) showed the highest transparency and uniformity to visible light. A mean grayscale value of 212 with a grayscale variation of 6 was found in the 0.3W-exposed window.

![Figure 4-39. Backlit microscope picture of a 200 × 200μm² window created by a 0.3W argon ion CW laser beam with a 10μm diameter spot in a Sn/Zn film.](image)

Figure 4-40 and Figure 4-41 show both Zn/Sn and Sn/Zn films’ relationship between the camera visible grayscale level and power. The corresponding grayscale mean and deviation values are shown in Table 4-24. Note that the two defects shown in Figure 4-40 are from the original films rather than for the laser exposure. Compared to Zn/Sn, Sn/Zn had a better OD profile for a grayscale material, but the former had a larger power range for grayscale writing. Figure 4-40 illustrates that both films had a similar slope: the percentage change per mW is 0.258 for Sn/Zn compared to 0.261 for Zn/Sn; however, Zn/Sn covered a larger power range than Sn/Zn: 0.07~0.3W compared to 0.07~0.2W, respectively. Note we need to obtain more measurements in order to determine the linearity of these two curves.
Figure 4-40. (a) Zn/Sn’s and (b) Sn/Zn’s backlit microscope pictures of five small windows created with various laser exposures (0.07W, 0.1W, 0.2W, 0.3W and 0.4W) with a 10μm diameter spot size

Table 4-24. The exposed Zn/Sn and Sn/Zn films’ visible light grayscale values

<table>
<thead>
<tr>
<th>Laser power (W)</th>
<th>0.07</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn/Sn Grayscale mean</td>
<td>37</td>
<td>58</td>
<td>179</td>
<td>252</td>
<td>255</td>
</tr>
<tr>
<td>Zn/Sn Grayscale deviation</td>
<td>9</td>
<td>11</td>
<td>48</td>
<td>8</td>
<td>2</td>
</tr>
<tr>
<td>Sn/Zn Grayscale mean</td>
<td>86</td>
<td>111</td>
<td>212</td>
<td>217</td>
<td>218</td>
</tr>
<tr>
<td>Sn/Zn Grayscale deviation</td>
<td>13</td>
<td>12</td>
<td>9</td>
<td>6</td>
<td>6</td>
</tr>
</tbody>
</table>

Figure 4-41. Zn/Sn and Sn/Zn’s camera grayscale levels of five small windows created with various laser exposures (0.07W, 0.1W, 0.2W, 0.3W and 0.4W) with a 10μm diameter spot size

4.6.2 UV/visible Spectrometer Analysis

As shown in Figure 4-42, after 0.07~0.4W laser beam scanning with 10μm spot, the OD for both Sn/Zn and Zn/Sn kept increasing, achieving over a 3 OD change, as the
power increased in the full power range (0-0.4W). These films achieved the best OD versus power relationship among all the investigated films.

In comparison, after 0.07-0.4W laser beam scanning, Zn/Sn’s OD dropped gradually until 0.4W where it saturated. Sn/Zn, on the other hand, showed a gentler slope, but also had discontinuities at 0.07W and 0.15W. We are not certain how repeatable those discontinuities are. In addition, shown in Figure 4-42, Zn/Sn achieved a slightly larger OD change than Sn/Zn after the same laser scanning (3.71 to 0.26 OD compared to (3.71 to 0.29 OD, respectively). This difference may relate to the refractive index of Sn (1.41) and Zn (0.60), so more laser energy could be reflected on Sn/Zn than Zn/Sn.

![Figure 4-42. OD response to laser power of the Zn/Sn and Sn/Zn films](image)

### 4.6.3 Profilometry Analysis

Compared to the exposed Zn/Sn film (Figure 4-43 (a)), the profilometry peaks in the exposed Sn/Zn (Figure 4-43 (b)) are smaller and increase more gradually with laser power. Table 4-25 shows the thickness range of the laser exposed areas in Zn/Sn and Sn/Zn films. In Zn/Sn, little thickness change occurred in the strips exposed by different laser powers, which may result from an uneven oxidation. Zn/Sn presented a similar roughness (with an average value of 8145Å) to the exposed Bi/Zn film (8275Å), which is the most rough among the investigated films.
Figure 4-43. (a) Zn/Sn and (b) Sn/Zn films’ profilometry results of the exposed areas created with various laser powers (0.07W, 0.1W, 0.2W, 0.3W and 0.4W) with a 10μm spot size.

Table 4-25. The Zn/Sn and Sn/Zn films’ thickness versus power

<table>
<thead>
<tr>
<th>Laser power (W)</th>
<th>0.07</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn/Sn thickness</td>
<td>800</td>
<td>755</td>
<td>750</td>
<td>650</td>
<td>650</td>
</tr>
<tr>
<td>thickness range (±Å)</td>
<td>3700</td>
<td>3725</td>
<td>2800</td>
<td>4600</td>
<td>5500</td>
</tr>
<tr>
<td>Sn/Zn thickness</td>
<td>300</td>
<td>500</td>
<td>600</td>
<td>875</td>
<td>950</td>
</tr>
<tr>
<td>thickness range (±Å)</td>
<td>2100</td>
<td>2550</td>
<td>2675</td>
<td>3175</td>
<td>3600</td>
</tr>
</tbody>
</table>

4.6.4 XRD Analysis

Figure 4-44 shows the XRD pattern for a Zn/Sn film. The height of peaks and the standard intensity are shown in Table 4-26. After scanning with a 0.2W laser beam with a 2μm diameter spot, other oxides, besides zinc and tin oxide, appeared. Note that the Zn/Sn film was the only investigated bimetallic film with a metal alloy (Sn0.85Zn0.15) in both the as-deposited and the exposed area. The shiny spots shown in the microscope picture (Figure 4-39) may come from this metal alloy material, which may be invisible with a metal Sn or Zn background, as in the as-deposited film, but they may appear with a transparent oxide background in the exposed area.
Figure 4-44. XRD pattern of Zn/Sn before (0W) and after exposure (0.2W, 2μm spot)

<table>
<thead>
<tr>
<th>Curve of unexposed area</th>
<th>Peak</th>
<th>Zn2SnO4 (220)</th>
<th>Zn(SnO3) (104)</th>
<th>Zn (101)</th>
<th>Sn0.85Zn0.15 (101)</th>
<th>ZnO (102)</th>
<th>ZnO (103)</th>
<th>ZnO (230)</th>
<th>Sn0.85Zn0.15 (102)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak height</td>
<td>281</td>
<td>140</td>
<td>60</td>
<td>98</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>Standard intensity (%)</td>
<td>62</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>90</td>
<td>29</td>
<td>60</td>
<td>7</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Curve of exposed area</th>
<th>Peak</th>
<th>Zn2SnO4 (220)</th>
<th>Zn(SnO3) (104)</th>
<th>Sn0.85Zn0.15 (101)</th>
<th>Zn2SnO4 (331)</th>
<th>ZnO (103)</th>
<th>ZnO (230)</th>
<th>Sn0.85Zn0.15 (102)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak height</td>
<td>70</td>
<td>161</td>
<td>28</td>
<td>45</td>
<td>5</td>
<td>5</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Standard intensity (%)</td>
<td>62</td>
<td>100</td>
<td>100</td>
<td>2</td>
<td>29</td>
<td>60</td>
<td>7</td>
<td></td>
</tr>
</tbody>
</table>

4.7 Comparison of the Investigated Films

This section compares the films for their capacities as masks for the grayscale laser direct-write process. The quality of each exposed film varies with the laser's parameters, so the discussion below is limited to the certain laser writing specifications we used. Therefore, may not show the best quality possible for each investigated material.
4.7.1 Minimum OD of the Exposed Films

The achievable transparency variation at UV wavelengths is critical for this research because it determines the number of grayscale levels that can be created in the masks. Table 4-27 gives the minimum OD created in each film. The minimum OD of 0.20 was found in a In/Zn (25/75nm) film, which also had a 3.00 OD change after a 0.8W laser beam exposure with a 2μm spot size.

<table>
<thead>
<tr>
<th>Film</th>
<th>Zn(200nm)</th>
<th>Zn(240nm)</th>
<th>Al/Zn(5/95nm)</th>
<th>Zn/Al(95/5nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum OD</td>
<td>2.84</td>
<td>3.74</td>
<td>2.52</td>
<td>3.08</td>
</tr>
<tr>
<td>Minimum OD (peak power density: W/μm²)</td>
<td>(0.19)</td>
<td>(0.010)</td>
<td>(0.010)</td>
<td>(0.640)</td>
</tr>
<tr>
<td>OD range</td>
<td>2.38</td>
<td>2.54</td>
<td>2.08</td>
<td>2.73</td>
</tr>
</tbody>
</table>

As shown in Table 4-27, the minimum OD obtained in the exposed Zn films was 0.46. The exposed Al/Zn, Zn/Al, Zn/Bi, Zn/Sn, Sn/Zn as well as the 95/5nm and 25/75nm In/Zn became more transparent at I-line than the exposed Zn films. This result proves our previous analysis that adding suitable materials to Zn followed by exposure to a laser can create grayscale masks with larger OD ranges than pure ZnO material.

4.7.2 OD Range of the Exposed Films

A maximum OD range over 3.4 at 365nm was found in several films. The 100nm thick Zn/Sn, after exposure to a 0.010W/μm² laser beam, had a 3.45 OD change, from 3.71 to 0.26. The Zn/Bi film exposed by a 0.002 W/μm² laser beam achieved a 3.58 OD change, from 3.93 to 0.35. Meanwhile, Sn/Zn, which was ranked highly for its sharp and clean exposed pattern seen in the microscope observation, also has a 3.42 OD range after exposure to a 0.010W/μm² laser beam.
Shown in Table 4-27 with a double border line, Zn/Al, Zn/Bi, Zn/Sn, Sn/Zn, as well as the 95/5nm and 25/75nm In/Zn have a large OD change while achieving a maximum OD > 3 and a minimum OD < 0.5.

### 4.7.3 OD Versus Laser Power Slope

Depending on the relationship between the OD change to laser power modulation, each film displayed a different ability for fine grayscale control. For a desired film, a linear or near-linear zone in the curve of OD versus power should occur over a range of both OD and power that is as large as possible.

Table 4-28 presents the OD and laser range for the near-linear part of each curve after scanning with 0~0.4W with a 10μm spot size. Note, the below comparison is limited to the power levels and range used.

<table>
<thead>
<tr>
<th>Film Type</th>
<th>Starting OD</th>
<th>Ending OD</th>
<th>OD change</th>
<th>Power range (W)</th>
<th>Slope (OD/W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200nm Zn</td>
<td>2.86</td>
<td>0.86</td>
<td>2.00</td>
<td>0.20</td>
<td>10</td>
</tr>
<tr>
<td>240nm Zn</td>
<td>3.86</td>
<td>1.26</td>
<td>2.60</td>
<td>0.20</td>
<td>13</td>
</tr>
<tr>
<td>Bi/Zn</td>
<td>3.51</td>
<td>0.41</td>
<td>3.10</td>
<td>0.12</td>
<td>26</td>
</tr>
<tr>
<td>Zn/Bi</td>
<td>3.70</td>
<td>1.10</td>
<td>2.60</td>
<td>0.20</td>
<td>13</td>
</tr>
<tr>
<td>In/Zn (5/5nm)</td>
<td>2.99</td>
<td>0.95</td>
<td>2.04</td>
<td>0.30</td>
<td>7</td>
</tr>
<tr>
<td>In/Zn (50/50nm)</td>
<td>2.80</td>
<td>0.46</td>
<td>2.34</td>
<td>0.40</td>
<td>6</td>
</tr>
<tr>
<td>In/Zn (75/25nm)</td>
<td>1.79</td>
<td>0.58</td>
<td>1.21</td>
<td>0.25</td>
<td>5</td>
</tr>
<tr>
<td>Sn/Zn</td>
<td>1.96</td>
<td>0.32</td>
<td>1.64</td>
<td>0.16</td>
<td>10</td>
</tr>
<tr>
<td>Al/Zn</td>
<td>2.52</td>
<td>0.44</td>
<td>2.08</td>
<td>0.30</td>
<td>7</td>
</tr>
<tr>
<td>Zn/Al</td>
<td>2.85</td>
<td>0.75</td>
<td>2.10</td>
<td>0.40</td>
<td>5</td>
</tr>
<tr>
<td>Sn/Zn</td>
<td>3.71</td>
<td>0.29</td>
<td>3.42</td>
<td>0.40</td>
<td>8</td>
</tr>
<tr>
<td>Zn/Sn</td>
<td>3.71</td>
<td>0.26</td>
<td>3.45</td>
<td>0.40</td>
<td>9</td>
</tr>
</tbody>
</table>

Using 0~0.4W scanning, in comparison, In/Zn (50/50nm), Zn/Al, Zn/Sn and Sn/Zn films (marked by a gray background), not only had 0~0.4W available power range, but they also had a shallow OD versus laser power slope (5~9 OD/W) that result in an OD change of 2.1~3.4. Bi/Zn shows a very steep slope (26 OD/W). In fact, both Bi/Zn and Zn/Bi have an unusual relationship of OD versus power, making their grayscale fine writings uncontrollable.
4.7.4 Smoothness and Uniformity of the Exposed Films

The morphological features of the oxidized films changed dramatically with the materials as well as the layer structure of these bimetallic films. The surface roughness of the exposed area was measured by profilometry analysis. Table 4-29 displays the film roughness comparison, which used the average value of the thickness change of the five small windows created by 0.07~0.4W laser beam exposure in each film. The 95/5nm, 50/50nm In/Zn showed the lowest surface roughness among all the investigated films. Zn, Zn/Al and Al/Zn had a relatively better surface than Sn/Zn, Zn/Sn, Bi/Zn and Zn/Bi bimetallic films. The average roughness of Bi/Zn was over 4 times of In/Zn films, presenting the worst surface quality among these investigated films after 0.07~0.4W laser beam scanning.

Table 4-29. The average surface roughness of the exposed films

<table>
<thead>
<tr>
<th>Film</th>
<th>Zn</th>
<th>Bi/Zn</th>
<th>Zn/Al</th>
<th>Sn/Zn</th>
<th>Al/Zn</th>
<th>In/Zn(50/50nm)</th>
<th>In/Zn(95/50nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2460</td>
<td>8275</td>
<td>3045</td>
<td>8145</td>
<td>2185</td>
<td>1800</td>
<td>1400</td>
</tr>
<tr>
<td>Average roughness (Å)</td>
<td>2460</td>
<td>8275</td>
<td>3045</td>
<td>8145</td>
<td>2185</td>
<td>1800</td>
<td>1400</td>
</tr>
</tbody>
</table>

In addition, from the grayscale standard deviation obtained by observation using a microscope, we determined that Zn has the most uniform visible transparency after 0~0.4W (10µm spot diameter).

4.7.5 Best Candidates for Grayscale Masks

The optical properties and surface roughness of each exposed film is a combined result of the film’s physical characteristics and laser writing parameters. The films were ranked differently in their optical characteristics and surface profiles. However, for a candidate used in laser direct grayscale materials, the optical characteristics of most importance are as follows:

(1) In order to achieve a high transparency at 365nm, the minimal OD of the exposed area must be very small, less than 0.5OD at 365nm.

(2) In order to achieve a large OD range, the unexposed area should be very absorbing. The maximum OD of the film is expected to be larger than 3 OD at 365nm.
(3) For fine laser writing control, the OD of the film should have an appropriate sensitivity to laser power. The steep and flat parts of the curve are expected to be as small as possible.

Zn/Al, Zn/Bi, Zn/Sn, Sn/Zn, as well as the 95/5nm and 25/75nm In/Zn, marked by the double lines in Table 4-27 and Table 4-28, fulfilled requirements (1) and (2); Zn/Al, Sn/Zn, Zn/Sn and 50/50nm In/Zn, shown in Table 4-28 with gray background, had an appropriate slope value in the OD versus power curves and met requirement (3). Note in Table 4-28, both Zn/Al, Zn/Sn and Sn/Zn were both had a large OD change up to 3.4 and a small OD change versus laser power slope around 5~9W/OD. These films gave the best results for laser direct-write grayscale mask application. Therefore, Zn/Al, Zn/Sn and Sn/Zn, are ranked as the best materials for laser controllable grayscale writing among this research.

4.8 Shelf Test

Figure 4-45 provides the result of a shelf test we preformed. The exposed Zn and Zn alloys films were put in an 85°C oven (Forma Scientific model 3237) for a shelf test that lasted for 10 continuous days. A beaker of water was set inside during the whole test period to keep the humidity of the environment high. The transmittance (%) of the films before and after the 10-day shelf test (ST) was tested and the plots are shown in Figure 4-45. As shown in Table 4-30, the transmittance variation for each film at 365 nm is slight; in fact, Zn/Bi did not change at all. Interestingly, after the shelf test, the transmittance at 365 nm for Zn/Sn and Zn/Al films increased, shown by positive numbers (marked by the double border lines) in the table. Note, these two films also are ranked as the best candidates for their promising optic properties shown after the laser scanning process.
Figure 4-45. Comparison of the exposed films’ transmittance before and after the shelf test (ST)
Table 4-30. Transmittance of films before and after shelf test

<table>
<thead>
<tr>
<th></th>
<th>Zn</th>
<th>In/Zn</th>
<th>Zn/Bi</th>
<th>Zn/Sn</th>
<th>Zn/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>T% (at 365nm) before ST</td>
<td>86.86</td>
<td>42.86</td>
<td>23.05</td>
<td>39.40</td>
<td>7.60</td>
</tr>
<tr>
<td>T% (at 365nm) after ST</td>
<td>82.65</td>
<td>41.86</td>
<td>23.05</td>
<td>44.20</td>
<td>8.15</td>
</tr>
<tr>
<td>Transparency change (%)</td>
<td>-4.21</td>
<td>-1.00</td>
<td>0.00</td>
<td>4.80</td>
<td>0.55</td>
</tr>
</tbody>
</table>

4.9 Summary

This chapter introduced the material analysis and morphology tests using a microscope, UV/visible spectrometer, profilometry, XRD and EDX. Optical images taken by the microscope showed exposed Zn films had the most uniform transparency to white visible light. Using the profilometry, we found the exposed In/Zn films had the smoothest surface while Bi/Zn produced the roughest surface profile among all the Zn and Zn alloy films scanned by a 0.07~0.4W laser with a 10μm spot size.

The XRD analysis and EDX investigation confirmed that laser scanning on bimetallic films involves an oxidization process. The extent of oxidation within a film depended on the laser power used for scanning. Based on the EDX results through SEM and STEM, a higher power provided a higher possibility to achieve a full oxidation within the whole film.

The most transparent area was found in a 25/75nm In/Zn film where, after exposure by a 0.8W laser beam with a 2μm spot size, the OD changed from 3.20 to 0.20. Zn/Al, Zn/Bi, Zn/Sn, Sn/Zn, as well as the 95/5nm and 25/75nm In/Zn were found to have a large maximum OD range (>3) with the minimum OD (<0.5), and Zn/Al, Sn/Zn, Zn/Sn and the 50/50nm In/Zn were found to have a large laser range available for grayscale writing. In conclusion, because Zn/Sn, Zn/Al and Sn/Zn satisfy the desired characteristics of OD change and OD change versus laser power slope, they were ranked as the film with the best capacity for accurate grayscale laser writing.

The shelf test result demonstrated the stability of the exposed films, which promises these films can be stored in normal conditions.
CHAPTER 5.
3D STRUCTURES PATTERNED BY GRAYSCALE PHOTOMASKS

5.1 Introduction

Grayscale photomasks have many transmission levels within a single plate, which enables the creation of 3D structures in photoresist using a single photolithographic exposure. The resolution and shape of structures are limited by the capacity of the masks used. For example, the height variation is dependent on the transmission range included in the corresponding mask.

This chapter presents a practical application of our thin film photomasks in the standard UV photolithography to create complex 3D structures. SU-8, a photoresist widely patterned by binary masks for IC creation, was patterned by our grayscale thin film masks. SU-8 photoresist and the process details are introduced in the following sections. This chapter concludes with the 3D structures we created in SU-8, which are catalogued by two different methods.

5.2 Photolithographic Process Using SU-8

SU-8 by MicroChem is an epoxy-based, near-UV sensitive, negative photoresist with high viscosity. It is mostly processed by a UV photolithographic process with a typical light source at the I-line wavelength. It was designed to generate high aspect-ratio straight-walled ICs, microfluidic devices and MEMS features [76] [77] [79].

5.2.1 SU-8 Patterning Process and Absorption Characteristics

A normal process of SU-8 patterning includes spin coating, a soft bake, an exposure, development, rinsing and a drying step. The formation of a strong acid during exposure and the catalyzing of the acid during the post exposure bake causes SU-8 to cross-link which increases its resistance to the developer [76]. The unexposed part is
removed and a reverse pattern of the photomask is created in the SU-8 after the development step [78]. SU-8 can produce ultra-thick structures, but the thickness of SU-8 used in this research was only 100µm or less because the absorption characteristics of SU-8 to UV light must be considered when it is used in patterning complex continuous tone structures.

A 365nm light source, recommended by MicroChem, is not the only wavelength that SU-8 is sensitive to. In fact, light with wavelengths shorter than 350nm are highly absorbed by SU-8 [78]. Ling et al [79] reported that penetration length (distance at which intensity decays to 1/e of incident intensity) at the wavelength of 330nm is 10µm, 356nm is 100µm, 380nm is 1000µm and 454nm is 10000µm [79] [80]. For I-line, Ling et al mentioned that the transmission at a depth of 10µm is over 90% while it drops to 70%~80% at a distance of 100µm. For this reason, the thickness of SU-8 was designed to be 100µm or less to remove the possibility of uneven absorption of SU-8. This way we ensure that the radiation difference is controlled by only the grayscale masks.

5.2.2 Topside and Backside Exposures

SU-8 can be exposed either directly on its top surface or indirectly through a transparent substrate. The first method (Figure 5-1 (a)) is called a frontside or topside exposure, and it is the most common way to expose photoresists. The second method (Figure 5-1 (b)) is called backside exposure, which is not as common in the literature [77].

![Figure 5-1](image-url)  
Figure 5-1. Two UV photolithographic exposure methods for SU-8 photoresist and the resulting 3D structures: (a) frontside exposure and (b) backside exposure
Because SU-8 is a negative photoresist, for an insufficiently exposed SU-8, only the upper surface is possible to be crosslinked and will remain after development, while the deeper regions are be removed by the developer because of insufficient exposure. This difference will generate suspended structures when it is exposed from its free surface (frontside exposure). As shown in Figure 5-1(a), if no pillars or any other supporting structures are present, the triangular structures will not stand upside down stably.

Figure 5-2 gives another example. A V-groove SU-8 feature (Figure 5-2(c)) on a Si substrate exposed from its free surface using a Zn/Al film mask. The mask pattern (Figure 5-2(b)) covered the maximum transparency (left) to the minimum transparency (right). This mask pattern was modified by a V-groove bitmap (Figure 5-2(a)). The exposed time is 45 seconds. The part of SU-8 exposed at a low intensity became partially cross-linked from the surface, resulting in only the top area of SU-8 remaining after development. As shown in Figure 5-2(c), without an anchor, this suspended thin skin fell down and created undesired structures.

![Figure 5-2. (a) a V-groove bitmap, (b) the Zn/Al pattern transferred from the bitmap and (c) the SEM picture of a frontside exposed V-groove SU-8 structure modified by the Zn/Al film mask](image)

For the same reason, insufficiently exposed pillars lost adhesion and were washed away by the developer, shown in Figure 5-3. These 4 pillars were part of a single row 16-square pattern (Figure 5-3 (a)). Due to underexposure, the left two square pillars were
moved away from their original spots. The right two square pillars, because of a sufficient exposure, were able to stick to the substrate stably.

Figure 5-3. SEM picture of SU-8 frontside exposed four-pillar feature (b), which was transferred from a single line 16-square pattern (a) created in SU-8 transferred from a patterned Zn/Al film

The parameters recommended by Microchem [113] are not suitable for our complex 3D structure creations. Afromowitz [77] patented the backside exposure method (Figure 5-1 (b)), by which V-groove structures with continuously curved surfaces and highly linear ramps (with up to a 1mm height) were fabricated [78], but the available information for SU-8 to be patterned by grayscale masks is very limited. The process parameters (summarized in Table 5-1) were found by iterating experiments with UV photolithography for patterning complex 3D structures.
<table>
<thead>
<tr>
<th>Process</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>DI water resin and N₂ blow purge;</td>
</tr>
<tr>
<td>Pre-treatment</td>
<td>Bake at 120°C for 15 minutes.</td>
</tr>
<tr>
<td>SU-8 coating</td>
<td></td>
</tr>
<tr>
<td>1st 30 seconds</td>
<td>500–1000 rpm;</td>
</tr>
<tr>
<td>2nd 30 seconds</td>
<td>1500–2000 rpm;</td>
</tr>
<tr>
<td>3rd 30 seconds</td>
<td>2000 rpm.</td>
</tr>
<tr>
<td>Soft bake</td>
<td>At 50°C: 2 minutes; Increase the hotplate temperature from 50°C to 95°C</td>
</tr>
<tr>
<td></td>
<td>with a ramp at 300°C/hr; At 95°C: 4 hours.</td>
</tr>
<tr>
<td>Exposure</td>
<td>30 to 50 sec.</td>
</tr>
<tr>
<td>Pre-exposure bake</td>
<td>At 50°C: 2 minutes; Increase the hotplate temperature from 50°C to 95°C</td>
</tr>
<tr>
<td></td>
<td>with a ramp at 300°C/hr; At 95°C: 3 minutes.</td>
</tr>
<tr>
<td>Development</td>
<td>3 to 6 minutes.</td>
</tr>
<tr>
<td>Dry</td>
<td>N₂ gas blow.</td>
</tr>
</tbody>
</table>

5.3 Three-Dimensional Structures Created in SU-8

As mentioned in chapter 4, Sn/Zn and Zn/Al films are two of the best candidates for laser direct-write grayscale masks, so they were chosen to be the photomask materials to pattern SU-8. Figure 5-4 shows some patterns created in Sn/Zn and Al/Zn films, covering the transmission from maximum to minimum, but with a different grayscale range. The discrete grayscale distribution is found in the step-stair pattern and 4×4 squares (Figure 5-4 (a) and Figure 5-4 (b), respectively). The ramp pattern (Figure 5-4 (c)) is a bitmap that continuously covers 8-bit grayscale levels, and, correspondingly, a certain continuous levels of transmittance is transferred to the photomask pattern in the Sn/Zn film, as seen in the backlit picture.

Figure 5-4. Bitmaps (first row) and backlit microscope pictures (second row) of patterns: (a) step-stair pattern in a Zn/Al film, (b) 4×4 square in a Sn/Zn film and (c) ramp in a Sn/Zn film.
Using a standard photolithographic process with the parameters (summarized in Table 5-1), grayscale patterns from the bimetallic thin films were transferred into SU-8. Both frontside and backside exposures were used in our experiments. The structures exposed by different methods have different characteristics, which determine their applications. These microstructures were influenced by many factors, from the process parameters to the SU-8 itself; however, the variations of shape and height of the 3D microstructures patterned by our thin film masks are a vivid way to demonstrate our thin films’ capacities in patterning complex features.

5.3.1 Structures Patterned by the Topside Exposure Method

As mentioned previously, the frontside exposure method is still suitable for creating certain complex 3D structures if appropriate anchors or posts are designed to support the grayscale structures.

Figure 5-5 shows a few 100μm thick microbridges produced in SU-8 patterned by the Zn/Al photomask with a single exposure (99 seconds) through the SU-8’s free surface. The bitmap (Figure 5-5 (a)) is composed of six linearly distributed V-grooves with different slopes. The leftmost V-groove has the smallest slope while the rightmost one has the steepest slope.

A 5-10μm skin formed because the very low transparency in the photomask, allowed a very low exposure dosage through the relatively dark regions of the mask. This skin may also be added by a very short penetration depth (around 10μm) to certain UV mask aligner’s wavelengths (those less than 350nm) [79]. Upon development, the
underlying unexposed part was removed, creating the bridge layer while the totally exposed part became the support pillars for the bridge. Note, depending on the thickness of the layer, the longest part of the bridge skin can be up to 200 µm.

Furthermore, the nature of our grayscale masks also allows the channel shaping. As shown in Figure 5-6 (a), through adjusting grayscale distribution of the mask, the channels in SU-8 can be altered to create bridges and arches with different sizes and shapes.

![Image of microstructures](image)

Figure 5-6. SU-8 microstructures created by a single frontside exposure method using the Zn/Al photomask: (a) microbridges with different slopes and (b) an embedded microchannel

In addition, because a microbridge and a microchannel are similar, the microbridge pattern can be simply widened so that our grayscale masks create microchannels, which are currently widely used in microfluidic devices. Figure 5-6 (b) presents an embedded microchannel patterned by the same Zn/Al bimetallic thin film mask with a single frontside exposure.

Using halftone binary photomasks to create complex 3D structures would require multiple exposures. For example, to create encapsulated micro-fluidic microchannels, a distinct exposure using 245nm and 365nm light sources was needed when patterned by a binary film mask [90]. Obviously, using our grayscale masks with a single exposure (365nm) is simpler and more efficient than using halftone binary photomask with multiple exposures [90].
5.3.2 Structures Patterned by the Backside Exposure Method

The backside exposure method can be used to create grayscale structures without requiring any supporting features. Insufficient irradiation will generate suspended features when using the frontside exposure method. Because of the relatively low radiation of the photoresist through the transparent substrate, a thin layer will remain on the substrate after development with no gap between the resist and the substrate. Thus, compared to the frontside exposure method, the backside method allows for more freedom in creating 3D structures.

Figure 5-7 gives an example. Figure 5-7 (c) shows a SEM picture of SU-8 microstructures patterned by a Zn/AI mask (Figure 5-7 (b)), which includes a V-groove transferred from an 8-bit grayscale bitmap (Figure 5-7(a)). The slope of the 3D groove structure is determined by the grayscale set intensity fade rate in the photomask. The three mask patterns for the three V-grooves (Figure 5-7 (c)) were transferred from the same bitmap (Figure 5-7(a)), but were written by different laser writing parameters.

![V-groove microstructure creation](image)

The mask pattern for the top V-groove, the largest of the three structures, was written at a faster writing speed than those used in creating the other two mask patterns. Additionally, the laser powers used to produce the thin film mask patterns for the two small V-groove structures were different, resulting in a different gap between the two strips. Common to all three structures is that they all have a continuous height variation,
which vividly reflects the linear grayscale distribution in the Zn/Al photomask. More examples using the backside exposure method are illustrated in Figure 5-8.

Figure 5-8. (a) the bitmap for the backside exposure of the staircase, (b) the fabricated staircase structure, (c) the bitmap for the backside exposure of the conical indent structure and (d) the fabricated conical indent structure

One is a multi-step staircase (Figure 5-8 (a) and (b)) and another is a conical indent structure (Figure 5-8 (c) and (d)). The 8-step stair case shows discretely distributed 8 grayscale levels, whereas the slope of the conical indent displayed the gradually increasing transparency distribution from the edge to centre in the mask pattern. These two structures also mirrored the influence of the development process in creating 3D structures. For example, the two dark horizontal lines shown in Figure 5-8 (a) were used to create protective walls, which prevent the lowest stair from washing away during
development. As shown in Figure 5-8 (d), the centre part became a U-groove shape instead of the desired V-groove, which may result from an insufficient developing.

Note, during the backside exposure process, the glass substrate was located between the photomask and photoresist (illustrated in Figure 5-1 (b)), so the diffraction of the exposure light within the glass slide may degrade the sharpness of the patterns transferred. To achieve a higher resolution of 3D structures, a new method was explored, in which SU-8 was directly coated onto the photomask film. As shown in Figure 5-9, SU-8 was directly coated on the photomask film and then exposed through the glass and the film mask.

![Figure 5-9. Backside exposure for SU-8 on a patterned film with a glass substrate: (a) UV photolithographic exposure process and (b) 3D structures on the film and glass substrate](image)

This method sacrifices the mask used, but the SU-8 layer can be exposed by the photomask directly without the influence of diffraction; therefore, the 3D structure is more precisely transferred than the way in which SU-8 was coated on a bare glass slide. In addition, the bimetallic masks are easy and cheap to fabricate, so this method will not add any obvious workload on producing new masks.

As shown in Figure 5-10, the 3D structures were transferred from the same film photomask, but the microstructures shown in the left column (Figure 5-10 (a) and (c)) were created in SU-8 on the mask film through a glass substrate and those in the right column (Figure 5-10 (b) and (d)) were generated in SU-8 on the mask. Obviously, the
3D structures created on the sacrificed photomask were much clearer and have sharper features than those created in SU-8 on glass.

![Image](image.png)

Figure 5-10. Backside-exposed SU-8 structures transferred from the same mask: (a) and (c) SU-8 on photomask with glass; (b) and (d) SU-8 on glass.

Note that the development process for SU-8 affects the shape and sharpness of the 3D structures. Therefore, an appropriate development process is required in order to precisely transfer the mask patterns to SU-8. After the developer and other parameters (e.g., temperature) are decided, the developing time is critical. However, the development time for 3D structures with different slopes and shapes are different. Therefore, to transfer patterns with various grayscale distributions precisely into SU-8...
with the same development time becomes challenging. Figure 5-11 displays some examples.

Figure 5-11. 3D structures created in SU-8 on a patterned film using backside exposure (exposure time: 30-50 sec) from patterns in a Sn/Zn film

An 8×8 matrix (Figure 5-11 (a)), two V-grooves (Figure 5-11 (b)) and two grating structures (Figure 5-11 (c) and (d)) with slope up to 60° were produced using the sacrificed photomask process. Note that different exposure times (30–50 seconds) were adopted to transfer the different bitmap patterns to the masks.

Obviously, for any pattern that includes different heights and slopes (e.g., an 8×8 matrix-pillar and a V-groove), a development time that guarantees that the entire set of
features develops properly is difficult to find. As shown in Figure 5-11(a), the development time that allowed the left top cubic pillar to have a flat top and straight walls, made the ones in the middle rows to have triangular and rough tops. Therefore, the shape of the matrix pillars cannot to exactly display the uniformity of each square in the corresponding mask. However, to a certain extent, the height difference of each column and certain rows showed the varying rate of the grayscale in the mask.

On the other hand, within the same development time, the two V-groove structures shown in Figure 5-11 (b) were created. One reason is the two slopes are similar, and another reason is the gap between the left and right part of each V-groove allows a sufficient chemical reaction between the developer and the SU-8. Therefore, we observed incomplete developing between closely spaced gratings (Figure 5-11 (c) and (d)).

Note, as shown in Figure 5-11, the height variation of the pillars, the different slope gradients (30~60°) of the linear ramps in the V-groove and gratings indicate that their corresponding mask patterns have different grayscale level fade rates, which demonstrate the capacity of the mask films for complex 3D microstructure fabrication.

5.4 Summary

Using a thick negative photoresist, SU-8, 3D microstructures with height variations up to 100 µm and slopes up to 30~60° were successfully patterned by the Zn/Al and Sn/Zn grayscale masks using standard photolithography. The various heights and slopes of the structures reflected the grayscale distribution of the thin film masks employed.

Both frontside exposure and backside exposure methods were adopted to create 3D microstructures with various shapes. The large OD range and high resolution grayscale patterns of our thin film masks allow microchannels, V-grooves and other microstructures with continuously-varying heights to be fabricated by a single exposure using UV photolithography. This process demonstrated the simplicity of using grayscale masks to create complex 3D structures over other technologies, including the binary mask patterning method.
In addition, for the first time, SU-8 was directly coated into the patterned film, allowing for the creation of higher resolution 3D structures than those created in SU-8 on a glass slide.
CHAPTER 6.
CONCLUSIONS AND FUTURE WORK

6.1 Thesis Conclusions

In previous research by our group, Dr. Glenn H. Chapman and several of his students demonstrated that a laser-induced partial oxidation process allows for cheap and fast production of grayscale photomasks on Bi/In and Sn/In bimetallic thin films, which have a typical OD change of 2.8 (3.00 to 0.22) at the I-line (365nm). This thesis explored Zn alloys as new bimetallic combinations.

100nm thick Zn alloy films, such as Sn/Zn, Zn/Sn, Al/Zn, Zn/Al, Bi/Zn, Zn/Bi and In/Zn, were first DC/RF-sputtered from two metal targets onto glass substrates. The deposited films were then raster-scanned with an argon ion CW laser at 488nm. To characterize each exposed film for application in grayscale photomasks, their surface was observed and material analysis was carried out using a microscope, UV/visible spectrometer, profilometry, XRD and EDX.

Optical images by the microscope showed that the exposed Zn films offered the most uniform transparency to white visible light. Using profilometry, the smoothest surface was found in the exposed In/Zn films. In addition, oxide peaks, which appeared in the XRD pattern of each film after laser exposure, confirmed that laser scanning on Zn alloy bimetallic films involved an oxidization process. EDX investigation through SEM and STEM showed that the extent of oxidation within a film depended on the laser power used for scanning.

Using the UV/visible spectrometer, the most transparent material at the I-line was found in a In/Zn (25/75nm) film, where the OD changed from 3.20 to 0.20 after a 0.8W (10μm diameter size) laser exposure. The maximum change in OD was shown in a 100nm Zn/Sn film, where the OD changed from 3.71 to 0.26. These films offer a greater range of transparency at the I-line than existing commercial chrome halftone binary and HEBS glass analog photomasks.
A large transmission range is desired for grayscale photomasks. Zn/Al, Zn/Bi, Zn/Sn, Sn/Zn as well as the 95/5nm and 25/75nm In/Zn meet the requirements of the maximum OD >3 and the minimum OD <0.5. To achieve controllable grayscale laser-writing in these photomask candidates, a near-linear relationship between OD and laser power is desired. Zn/Al, Sn/Zn, Zn/Sn and 50/50nm In/Zn were found to have a large laser range with almost linear characteristics for grayscale writing. Because Zn/Al, Zn/Sn and Sn/Zn have a shallow OD versus laser power slope (5~9 OD/W) over a 0.4W range while achieving a large OD range of 3.45, these films are considered the best candidates for laser direct-write grayscale photomasks.

To check the practicality of these Zn alloy films in the UV photolithographic process, 3D microstructures were patterned in Sn/Zn and Zn/Al thin film grayscale masks. Microbridges with height variations up to 100μm and V-grooves with angle variations around 30°~60° were created in SU-8 using only a single exposure, demonstrating the efficiency of Zn alloy thin films for creating 3D microstructure in standard UV grayscale photolithographic technology.

6.2 Suggested Future Work

Although this research has provided integrated steps for grayscale writing in bimetallic films, future research is needed to improve the process and material characteristics.

6.2.1 Improving Film Smoothness

In this research, we used a multi-scan process to expose a Zn single layer film with several laser powers and found a 63% reduction on roughness of the exposure area compared using with only a single exposure. In the future, this process is suggested for bimetallic films. The speed and line spacing of the writing laser should be adjusted to achieve a smoother surface of exposed films.

6.2.2 Hard Protection Layer

In our group’s previous research, the spin-on-glass technique was applied on the SiO₂ layer as a protection layer for the bimetallic films, but we did not use this step.
because cracks formed during the laser scanning process. Relatively, the deposition technique can create more even and thinner films than the spin coating process.

An initial experiment was carried out on an Al/Zn (15/85nm) thin film, on which a 10nm thick SiO$_2$ film was deposited. The OD of a glass slide with the same thickness of a SiO$_2$ film is 0.046, which is similar to the OD of a blank glass slide (0.048OD). After separately scanning by 0.1W and 0.2W through a 50× lens, the OD drops to 0.36 and 0.2 OD, respectively, from the original 2.27 OD. More importantly, no cracks formed after the high laser exposure on the film with this sputtered-SiO$_2$ protection layer. Because of the high transparency at UV and the high hardness, the sputtered-SiO$_2$ film is a promising protection layer for our bimetallic thin films.

Further research should explore this coating process.

6.2.3 New Composition Ratio and Materials

In this research, except In/Zn, other bimetallic films had a fixed composition ratio. In the future, various ratio and multilayer (more than two layers) structures are suggested.

In addition, Mg and Cr are also two promising candidates to form ZnO-based thin film photomasks. The bandgap of Mg-joined ZnO was reported as high as 4.0eV [88]. Cr, on the other hand, is widely used in binary photomasks for its high stability, high hardness and high transparency to UV light. In this research, Cr/Zn (10/90nm) was deposited for an initial experiment. Through a 50× lens exposure, a 0.05W-exposed and a 0.3W-exposed area had a 0.35 OD and 0.09 OD, respectively, changing from its original 3.02 OD. These results demonstrate a very promising optical property desired for masks in UV photolithography.

6.2.4 Thermal Modelling

In our ANSYS modelling of laser radiation on metal films, the optical and thermal characteristics of films were assumed temperature-independent and constant during laser illumination because of the unavailable database. This simplification is inconsistent with the physical experiments, where original opaque thin films become transparent metal oxides. Setting appropriate material properties can improve the simulation accuracy.
However, the corresponding transition parameters with temperature or time as variables are not available for our particular films. Even the literature [57] shows that the critical temperature for some metal films (e.g., In and Sn), vary with the preparation process of the films.

Fortunately, the real-time optical characterization of the laser oxidization process in our group [89] provided the accurate time when the thin films become transparent during certain laser radiations. This accurate time would make a more reliable ANSYS simulation possible in the near future.

6.2.5 EDX Analysis

Energy-dispersive X-ray spectroscopy investigates the element distribution in both the surface and the inside of films. In this research, this analysis was the only technique that was able to show the oxygen distribution within the observed film as well as the depth of the oxidizing process through the material. Unfortunately, because of time and facility limitations, this analysis was only investigated by a visiting scholar who left before the full process was completed. For future work, a full EDX analysis that includes all reported elements and the corresponding amount numbers are needed.
APPENDIX

The table below shows the typical steps for an ANSYS transient thermal solid model, which was used to simulate temperature distribution of the Al/Zn and Zn/Al films during a laser exposure.

ANSYS 8.1 operations for a transient thermal solid model for Al/Zn and Zn/Al films

<table>
<thead>
<tr>
<th>General steps</th>
<th>Type</th>
<th>Operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preference</td>
<td>—</td>
<td>Thermal</td>
</tr>
<tr>
<td>Preprocessor</td>
<td>Element type</td>
<td>Thermal solid/Axi-har 4 node 25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Thermal solid/Axi-har 8 node 83</td>
</tr>
<tr>
<td>Modelling</td>
<td>Create/area/rectangle/by dimension</td>
<td>Material prop/material</td>
</tr>
<tr>
<td>Meshing</td>
<td>Meshing attributes/picked area/material type &amp; element type</td>
<td>Size control/manual size/lines/all lines/element edge length</td>
</tr>
<tr>
<td></td>
<td>Meshing tool/mesh/pick all/maps</td>
<td></td>
</tr>
<tr>
<td>Solution</td>
<td>Analysis type</td>
<td>New type/transient</td>
</tr>
<tr>
<td></td>
<td>Solution control</td>
<td>Automatic times stepping (5e-4 second)</td>
</tr>
<tr>
<td>Define load</td>
<td>Apply/thermal/temperature/on nodes/298K</td>
<td>Apply/thermal/heat flux/on line(2.3e-8)</td>
</tr>
<tr>
<td></td>
<td>Apply/initial condition/define/temperature/all nodes/298K</td>
<td></td>
</tr>
<tr>
<td>Solve</td>
<td>Current LS</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>FSI setup</td>
<td>Iteration/maximum step(1000)</td>
</tr>
<tr>
<td>General Postprocessor</td>
<td>Read result</td>
<td>Last step</td>
</tr>
<tr>
<td></td>
<td>Plot result</td>
<td>Contour plot or vector plot</td>
</tr>
</tbody>
</table>
REFERENCES


[58] M. Oh, S. Kim and T. Seong, “Growth of nominally undoped p-type ZnO on Si by pulsed-laser deposition”, Applied physics letter 87, 122103, 2005


[65] JCPDS version 2.14 PDF-2 database (sets 1-43), copyright (c) 1987-1993 JCPDS-ICDD Newtown Square, PA 19073, the USA, 1993.


