# Single Step Direct-Write Photomask Made From Bimetallic Bi/In Thermal Resist

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## ABSTRACT

A new single step direct-write photomask process has been proposed by using Bi/In bimetallic thermal resist which turns almost transparent with high energy laser exposure. The Bi over In metallic films, each layer ~40 nm thick, were DC-sputtered onto quartz mask plate substrates in a single pump-down chamber. Before laser exposure the Bi/In had 2.91 Optical Density. Bi/In is a bimetallic thermal resist and hence shows near wavelength invariance exposure sensitivity from Near IR to UV light. For Bi/In exposure, up to 0.9 W Argon laser (514 nm) beam was focused by an f=50 mm lens to a 10 micron spot. When writing a mask the Bi/In coated sample was placed on a computer-controlled high accuracy X-Y table and the pattern was raster-scanned by the laser at 10mm/sec. After exposure the Bi/In film became nearly transparent (0.26 OD) at I-line (365 nm) wavelength, and remained conductive. Bi/In photomasks have been used together with a standard mask aligner to pattern the oxide and Al layer during the manufacturing of test solar cell devices in the lab. Experiments also showed that annealing the as-deposited films at 90°C before laser exposure increase the Bi/In transparency.

Keywords: Direct-write photomask, Thermal Resist, Bimetallic Thin Film.

## 1. INTRODUCTION

Previous research has found that bimetallic layers of Bismuth on Indium creates an inorganic thermal resist with many interesting properties[1,2,3]. When exposed to laser pulses at energies equal to that of organic resists the Bi/In film is converted into a new material with quite different characteristics from the unexposed areas. It is chemically different enough that development in a diluted RCA2 solution ($HCl:H_2O_2:H_2O=1:1:48$) removes the unexposed areas with an excellent etch selectivity[4]. The remaining resist is also highly resistant to alkaline-based anisotropic silicon etching[3]. Yet potentially even more useful is the extremely large change in the optical absorption with the exposed areas becoming nearly transparent[1]. This suggested the possibility of using Bi/In resist as a direct write photomask.

Photomasks with smaller features, better controlled linewidth, fewer defects and lower cost are required by the microfabrication and micromachining industries. A conventional photomask consists of an insulating/transparent substrate, and a surface covering/patterning film, most commonly Cr. While quartz and glass have been widely used for decades as the mask substrates, many different kinds of materials have been used as the surface imaging layer. Drexler [5] heated up the exposed silver-halide emulsion to 250°C and the emulsion became visually transmissive to yellow-orange light in both silver and non-silver clear areas, but opaque in the silver areas to ultraviolet wavelengths. CrO, CrON, MoSi and MoSiON have been reported to be used to make single-layer attenuated phase-shift masks[6,7].

However Cr has been the most widely used covering materials in the wafer fab industry[8,9,10]. The typical Cr photomask manufacturing process involves the blank mask preparation: Cr and Cr oxide deposition, photoresist coating, resist baking, laser or e-beam direct-writing, resist development, metal layer dry or wet etching, resist stripping and cleaning[8,9]. There are many issues with current photomask and its preparation processes. Firstly, it is difficult to minimize the defect counts, as there are 5 – 9 operation steps involved in making a photomask and each step can introduce process defects and particles. Secondly, mask damage from ESD (electrostatic discharge) has long been a concern. Although a lot of effort has been spent in making the photomask and the pellicle set conductive by adding conductive films, conductive frames, conductive dust pellicles, etc.[10,11], ESD damage can be more problematic due to the shrink of the feature size. To make things even worse is that masks for 157 nm lithography will be kept in ambient atmospheres nearly free of water, which will increase the risk of ESD damage to masks[12]. Thirdly, although Cr dry

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etching has become a standard mask making process step, the loading effect is still a serious problem. The chrome etch rate changes with the ratio of clear area to opaque area on the mask, which can seriously affect the precise Critical Dimensions (CD) control[13]. Fourthly, the cost of masking is escalating. A 0.18 μm binary photomask for critical layers costs $8000 – 22,000, and those for non-critical layers cost $18,000 - $20,000. OPC (Optical proximity correction) and PSM (phase shift mask) add substantially to these prices[14]. In order to solve all these issues people in the semiconductor industry have to explore new processes and new materials. Takaoka, et al[15], proposed a sol-gel combined with DTR (diffusion transfer) process. A liquid containing metal oxide was applied to the substrate, and this dried and heated coating would act as a physical development nucleus layer into which the silver complex compound was diffused to form a silver film at the unexposed area. Plasma etching is not necessary. However it still involves more than 5 steps.

In this paper, a novel single step direct write photomask made from bimetallic Bi/In thermal resist is reported. Unlike conventional mask lithographic steps for patterning, Bi/In itself is a thermal activated optical material, hence patterns can be directly written onto the film, and the exposed Bi/In area becomes more transparent. Mask defects can be drastically reduced due to much fewer steps are needed in the preparation process. Moreover because both the exposed and unexposed Bi/In are conductive, there is inherently not ESD problem with this type of photomask. Obviously the manufacturing cost of Bi/In photomask is much lower than conventional masks. Bi/In is a potential photomask material for semiconductor industry. This paper investigates the resist itself to create a V-groove solar cell, and briefly looks at the mechanism behind the large optical changes.

## 2. Bi/In BIMETALLIC THERMAL RESIST

The Bi/In bimetallic resist concept (see Figure 1(a)) starts with the deposit of two thin (15-150 nm) film layers of materials whose combined phase diagram contains a eutectic, an alloy with a melting point local minimum below that of either metal[16]. The Bi/In phase diagram has a eutectic of 72°C at 22% bismuth and a local temperature minimum of 112°C at 53% bismuth[17]. In the resist the two film ratios are chosen to match these eutectic compositions. When exposed to a short laser pulses of ~7 $mJ/cm^2$ under a photomask or direct laser writing (Figure 1(b)) the exposed area will absorb the light energy and with sufficient power heat up to above the Bi/In eutectic temperature. At the end of the laser pulse, the resist layers will cool and solidify as the altered alloy. The material in the unexposed area, where the light is blocked by the photomask, will remain the same as two-layer structure. Tests show that the alloy have different chemical and optical properties than Bi or In. In resist applications two development etch solutions have been found[4] which will attack the areas of unexposed resist more aggressively than the exposed areas. As Bi/In film gets very transparent after high power laser exposure, which makes it material for making direct-write photomasks[2] and development is not needed.

The BiIn bimetallic films were prepared on glass slides and quartz using a Corona DC sputter machine that has 5 targets installed and can deposit multilayer films without an air break, creating the structures of Figure 1(a). The target materials used are two inches in diameter 99.99% Bi and 99.99% In. The substrates were RCA1 and RCA2 cleaned before deposition, and then baked for 20 minutes at 120°C to remove moisture. The vacuum chamber was pumped down to a base pressure of $6\times10^{-7}$Torr before sputtering. During deposition, the chamber pressure was kept at 4mTorr with an Ar gas flow rate of 10 sccm. The deposition rate for the bismuth, and indium was determined, as shown in Table 1, by

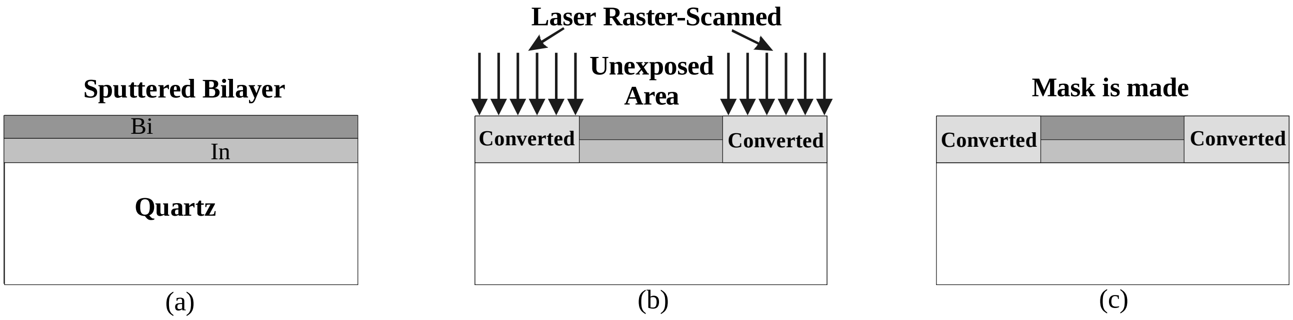

Figure 1. The mask making process steps. (a) Bi and In are DC-sputtered on quartz or glass with a bilayer structure. (b) Bi and In form an alloy when exposed to laser, and the unexposed area remains to be bilayer structure. (c) The exposed area becomes transparent after laser exposure, the unexposed Bi/In is opaque. The mask is then made.

Table 1. Bi and In Sputter Rate

| Metal | Argon Pressure | DC bias | Current | Watt·Min | Deposit rate Å/W·min |
|---|---|---|---|---|---|
| Bi | 4mTorr | 470V | 0.23A | 2500 | 12 |
| In | 3mTorr | 450V | 0.23A | 2500 | 4 |

sputter depositing thick films on glass slide substrates for 2,500W·min and measuring the film thickness with a KLA-Tencor AS5 profilometer.

Since the In sputter rate (4Å/W·min) was lower than that of Bi (12Å/W·min), a different sputter power was used for Bi and In sputtering in order to give a better control of film thickness. To prepare a 40nm/40nm BiIn film, the DC voltage was 500V and the current was 0.2A to sputter In, and to sputter Bi, the DC voltage was 350 V and current was 0.07A. The actual DC sputter powers for the Bi and In depositions were 24.5W and 100W, respectively.

The properties of the deposited films are very stable. Reflection and transmission measurements were made on a daily basis for three bilayer samples held at room temperature, under a 60W light bulb (about 10cm away) and immersed in a bath of liquid nitrogen (77°K). The reflection and transmission were measured on both the front (exposed to air) and back (on the glass substrate) surfaces, no significant changes were observed in transmission or reflection in any of the samples. A rigid shelf lifetime test has been carried out at 50°C and >90% humidity condition for over 200 hours, and no changes of the sample properties were observed[1]. Such stability is very important for photomasks.

## 3. LASER EXPOSURE

While Bi/In is a sensitive thermal resist much lower power is needed to create an etch resistant material with some transparency for a resist, while higher powers are required to maximize the change in optical characteristics. Also as a thermal resist Bi/In is wavelength invariant in laser exposure energy required for the reaction[3] Hence in this application an Argon CW laser running at 514 nm was used to expose the Bi/In films. The 2.5 mm diameter laser beam was focused by different lens (5×, 50× objective lens and 50 mm lens, dependent on the feature size) onto the sample to create higher power densities.

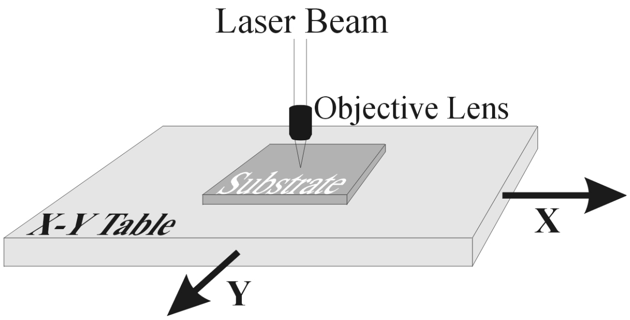

Figure 2. Exposure setup. The laser beam was focused by a 50 objective lens. The sample was placed on an X-Y table, while the laser beam was fixed.

The waist of the focused beam is from 2 μm to 10 μm. The laser beam was fixed during the scanning. The sample was placed on a computer-controlled high precision (±0.1μm) X-Y Z table, and the table moved back and forth along X direction at a constant speed, with a small incremental step along Y direction after each scan (Figure 2). Thus the laser beam raster-scans the sample to make a pattern. Different patterns can be made by writing computer control scripts or by using our proprietary table control software which takes bitmap image as the input file and the X-Y table will move accordingly so that the same image can be written on the sample. Three parameters contribute to a successful mask making: table moving speed, laser power and Bi/In film thickness. The table moving speed is similar to the exposure time in steppers or aligners. In the experiment it was kept at 1 cm/sec. The power of the Argon laser used for the scanning is from 0.3W to 0.9W when using 50 mm lens. The film thickness chosen is 40 nm / 40 nm.

When the laser beam hits the bilayer film part of the light will be reflected at each interface, and some light will be absorbed and converted into heat and the rest will transmit through the film. It is the absorbed portion of the light that exposes the film by heating up the metal. At laser powers above the threshold for reaction the physical and chemical properties of converted Bi/In films change and most importantly for masks it becomes almost. transparent compared to the unexposed Bi/In[1]. As covered in section 8 the heat converts the Bi/In into an transparent alloy or alloy oxide[18], while the unexposed area remained bilayer structure. Figure 1 shows the two steps to make a Bi/In direct-write photomask. Step 1 is the blank mask preparation: Bi and In are deposited onto quartz or glass substrate. Step 2 is the laser raster-scan: exposed area gets converted and turns to be more transparent, and the unexposed remains the same. In order to protect the pattern a protection layer such as SiO2 can be sputtered onto the mask surface after the pattern writing.

## 4. OPTICAL CHARACTERISTICS OF Bi/In FILMS

The large optical property difference between the exposed and unexposed bimetallic thermal resist Bi/In films is attractive since this can be utilized in many fields such as optical storage and direct-write photomask materials. It is observed that the light transmission increases rapidly with the laser exposure power. To characterize the optical properties of Bi/In films before and after laser exposure a Varian CARY 3E spectrometer was used to measure the absorption through the Ar CW raster scanned area and the unexposed area on the film. Figure 3 shows the Optical Density (OD) versus the transmission light wavelength for a 40 / 40 nm Bi/In film on a glass slide after exposure to Ar laser of different power. The top curve is the as-sputtered 40 / 40 nm Bi/In film, which is around 2.6 – 2.8 OD from 400 nm to 800 nm wavelength. The second, third and fourth curves are the OD's of films exposed to Ar laser of 300, 450, and 600 mW, respectively. As the power of the laser exposure increases, the OD of the exposed area reduces, and saturates at a minimum level where all of the material in the layers is converted. The absorption spectrum for the converted layers in the range from 400 nm to 800 nm reaches a minimum value of less than 0.1 OD at an exposure intensity of 600 mW. This shows a change in the OD of larger than 2.5 orders in terms of transmitted light power. An ideal direct-write photomask for i-line applications should have ~ 3 OD for unexposed area and < 0.25 OD for exposed area. The OD of unexposed 40/40 nm Bi/In at 365 nm (i-line) is 2.94 and that of area exposed with 600 mW Ar laser is 0.43. In order to improve the transparency of the exposed area while keeping the OD of the unexposed area, many methods are under investigation, such as adding different gases and elements during film sputtering, various substrate temperatures during exposure, finding the optimized film structure (thickness and order of deposition), etc.

It is found that annealing the Bi/In samples at 50 to 90°C for a period of time in the air before laser exposure helps reduce the optical density of the exposed area. An experiment comparing the OD of the oven-annealed and non-annealed samples was carried out. Two different Bi/In samples were used: one was 40/40 nm and the other was 15/15 nm film, all deposited on glass slides. Each sample was cut into 2 halves for comparison. One half was Ar laser scanned as-deposited and the other half was heat-treated at 90°C for 72 hours before laser scanning. In this way the influence of the fluctuation of film thickness from sample to sample was eliminated. Table 2 lists the OD comparison experiment results measured at i-line wavelength. The "Laser Power" column shows the Ar laser power that was used to expose the films. The "OD (Non-annealed)" column shows the OD of the films that were exposed as-deposited with different laser power. The "OD

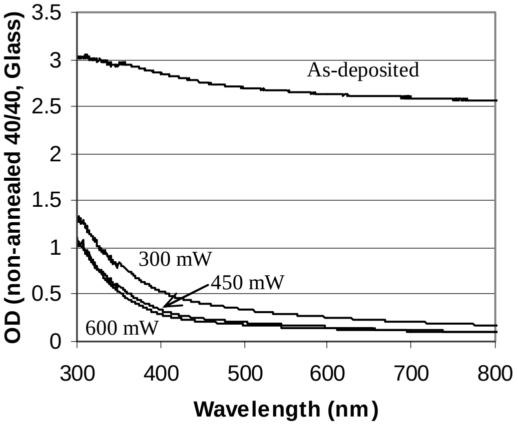

Figure 3. Optical absorption (300 nm to 800 nm) through 40/40 nm (non-annealed) Bi/In deposited on glass slide exposed by Ar laser with different power. From top to bottom: 0, 300, 450, and 600 mW. The sample was not heat-treated.

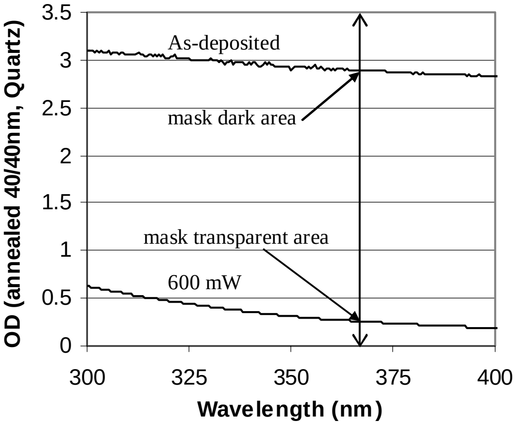

Figure 4. Optical absorption through annealed 40/40 nm Bi/In on quartz substrate, in the range of 300 nm to 400 nm. The top curve is the OD for unexposed, and the bottom is exposed with 600 mW Ar laser.

(Annealed)" is the OD of the films that were first heat-treated and then exposed with different laser power. The last column shows the percentage of OD reduction from non-annealed films. One can see that the OD of 40/40 nm film after 600 mW laser exposure dropped 8.42% from 0.435 to 0.398, while the unexposed area only dropped 0.81% and was still above 2.9. Similar results were also found for 15/15 nm films, although the OD drop for unexposed area (23.21%) was much larger than that of 40/40 nm film. The annealing mechanism that brings down the OD of films both before and after exposure is not fully understood at this moment. As the optical absorption of glass slides start to increase rapidly after 450 nm wavelength, Bi/In was deposited on quartz substrates in order to make photomask for i-line applications. Tests showed that with quartz as the substrate the OD of exposed area was 0.260 and unexposed area 2.911 at 365 nm wavelength. Figure 4 shows the OD of unexposed and 600 mW laser exposed area of annealed Bi/In on quartz sample in the wavelength range of 300 nm to 400 nm. It is also seen that the optical absorption of annealed quartz sample at 300 nm is much lower than that of non-annealed glass sample.

Table 2. Comparison of Optical Density (OD @ i-line) between oven-annealed and non-annealed Bi/In films deposited on glass slides.

| Film Type | Laser Power (mW) | OD (Non-annealed) | OD (Annealed) | OD Reduction % |
|---|---|---|---|---|
| **40 / 40 nm Bi/In** | 0 | 2.936 | 2.913 | 0.81% |
| | 300 | 0.726 | 0.515 | 29.13% |
| | 450 | 0.492 | 0.431 | 12.34% |
| | 600 | 0.435 | 0.398 | 8.42% |
| **15 / 15 nm Bi/In** | 0 | 1.142 | 0.877 | 23.21% |
| | 75 | 0.504 | 0.499 | 0.98% |
| | 150 | 0.299 | 0.266 | 11.18% |
| | 300 | 0.227 | 0.155 | 31.84% |
| | 450 | 0.170 | 0.158 | 7.14% |

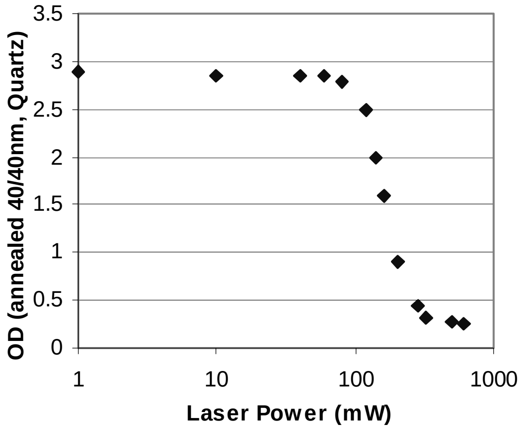

Figure 5. 40/40 nm Bi/In film optical absorption vs laser power at wavelength 365 nm. Absorption drops drastically at around 100 mW laser power and gradually saturates after 300 mW. The film was deposited on quartz and was annealed at 90°C for 72 hours.

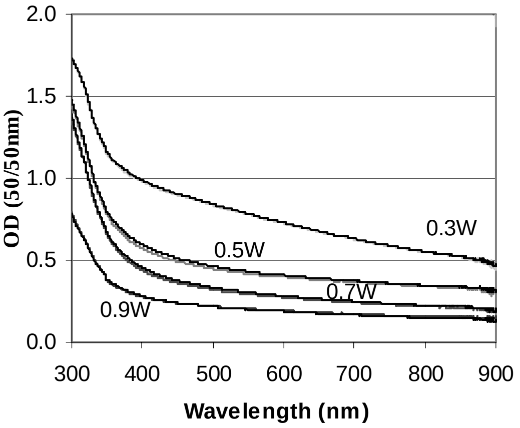

Figure 6. Optical spectrum before and after the shelf test. The spectrum lines before and after the shelf test overlap with each other, showing that the film optical property is stable.

Figure 5 shows a curve of optical absorption versus laser writing power at the wavelength of 365 nm which is very important for determining the direct write laser power requirements. It is noticed that when the laser is below 50 mW the Optical Density (OD) of the film does not change. The X-Y table moves with the speed of 10 mm/sec and the laser beam is focused to a small spot with 20 µm in diameter with 50 mm lens, hence 50 mW of Ar laser power yields around 5J/cm$^2$ power density (for exposure times of milliseconds). Converted masks are stable to exposure during mask use as the mask making powers are much higher than typical industrial exposure power density (10 – 100 mJ/cm$^2$) and While the exposure times is much shorter. Thus in mask applications the Bi/In temperature is raised far less than during the mask making exposures, thus the photomask stability and reliability will be maintained. The absorption drops sharply around 100 mW writing power, and it quickly saturates from 300 mW onwards and the optical density stabilizes around 0.26 OD on quartz substrates. With such low absorption levels the Bi/In resist has met the needs for a direct write photomask for 365 nm applications where the converted areas can directly be used as the mask “openings” without development. Both the unexposed and exposed films were reported to be very stable[2]. A shelf test was carried out in order to test the stability of the exposed area. The Bi/In films raster-scanned with different Ar laser power were kept in an environment of 70°C and ~100% humidity for 7 days. The optical spectrum was measured before and after the shelf test. As shown in Figure 6, the spectrum curves before and after the shelf test overlap each other. The transmission rate barely changed and the optical property is stable as is required for photomasks.

## 5. ELECTRICAL PROPERTIES OF Bi/In

Electrostatic discharge damage in conventional chrome masks is caused by the charge accumulation in the transparent non-conductive quartz area. Although a lot innovative technique has been applied to alleviate the problem, it is extremely difficult to eliminate ESD. However, Bi/In direct-write photomasks are free from ESD problem as both exposed and unexposed Bi/In films are conductive, which cover the whole mask surface. The sheet resistance of the exposed and unexposed samples was measured using a MP0705A four-point probe from Wentworth Labs, which is connected to an HP 3478A multimeter. The bilayer film was sputter-deposited on glass slides with 30 nm equally thick Bi on top of the In layer. The sheet resistance was first measured on the unexposed Bi/In film (named as Bi/In 30/30 U in Table 3), and then on the Ar laser raster-exposed areas (as Bi/In 30/30 E in Table 3). The laser power was 0.20W. The resistances of single layer Bi and In films of thickness 15 nm, 30 nm, and 45 nm were also measured. It is noticed that the resistivity of the thinner Bi and In films is higher than that of bulk materials, dropping significantly as the films get thicker. This can be attributed to the fact that the oxidized part of the film is more significant in thinner films than in thicker films. It is noticed that the exposed films are slightly more conductive that unexposed films.

Table 3. Sheet resistance and resistivity

| | Bi (15nm) | Bi (30nm) | Bi (45nm) | In (15nm) | In (30nm) | In (45nm) | Bi/In 30/30 U | Bi/In 30/30 E |
|---|---|---|---|---|---|---|---|---|
| Sheet resistance (Ω/sq) | 484.7±39 | 171.0±13 | 79.6±5 | 32±3 | 9.3±0.9 | 3.5±0.2 | 82.8±6 | 80.8±5 |
| Film resistivity (Ωcm) | $7.27\times10^{-4}$ | $5.13\times10^{-4}$ | $3.58\times10^{-4}$ | $4.91\times10^{-5}$ | $2.79\times10^{-5}$ | $1.56\times10^{-5}$ | $4.97\times10^{-4}$ | $4.85\times10^{-4}$ |
| Bulk resistivity (Ω cm) | $1.3\times10^{-4}$ | | | $8.0\times10^{-6}$ | | | - | - |

## 6. PREPARATION OF Bi/In DIRECT-WRITE MASK

To demonstrate that the Bi/In bilayer film can be used as a direct write material for practical fabrication applications, several photomasks have been made on glass slides and quartz substrates. Figures 7 – 11 show a mask made with the following conditions:

- 40 / 40 nm Bi/In deposited on quartz;
- Heat treated for 72 hours at 90°C (open air);
- Argon laser raster-scan power = 600 mW;
- 50 mm lens used to focus Argon laser before hitting the film, beam size = 10 μm;
- X-Y table moving speed (along X direction) = 1 cm/sec;
- Raster-scan increment (along Y direction) after each scan = 8 μm.

Figure 7 is a front-lit picture of the whole 1×1.6 cm direct-write Bi/In photomask. The laser-scanned areas are darker that the unexposed area from the front-lit picture. Figure 8 is a back-lit image of the mask, showing clearly the patterns. Figure 9 is an enlarged front-lit picture showing one of the patterns of 51μm line and space exposure structure. Figure 10 was taken with both front and back lights on, showing vertical lines in the exposed area that were generated by the laser raster-scan for a 25 μm line and space test structure. However, the raster-scan lines disappeared when only the back-light was on, as shown in Figure 11, and are not visible in exposed regular organic resist patterns from this masks (refer to Figure 12). One can also clearly see the smallest feature in the back-lit picture which is a 2 μm wide space. This width is really only the limits of the mask creation program not that of the resists.. Although we have not carried out experiments to find out the smallest feature size possible with the Bi/In film, TEM (Transmission Electron Microscopy) analysis showed that the grain size of the Bi/In film is 150 nm, indicating that the smallest feature can be ~ 150 nm[18]. In order

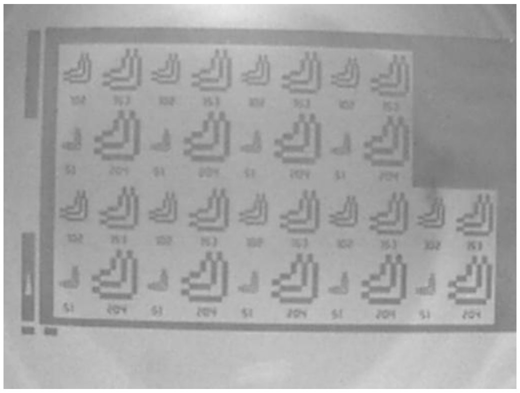

Figure 7. Front-lit picture of the 1×1.6 cm direct-write photomask made on a quartz plate coated with 40/40 nm Bi/In. The bilayer film was heat-treated for 72 hours at 90°C before laser exposure.

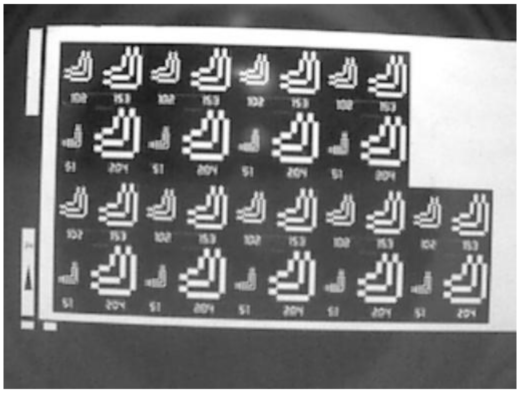

Figure 8. Back-lit image of the same mask in Figure 7.

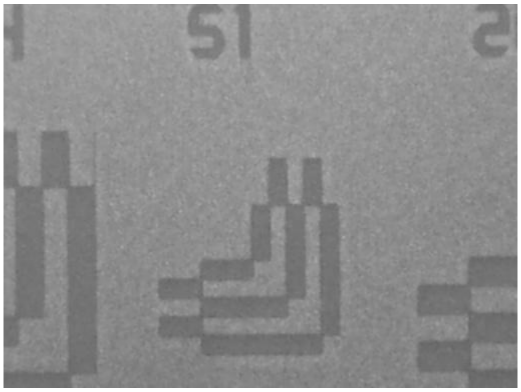

Figure 9. Enlarged front-lit picture of the direct-write photomask The width of the line at the middle is 51 μm.

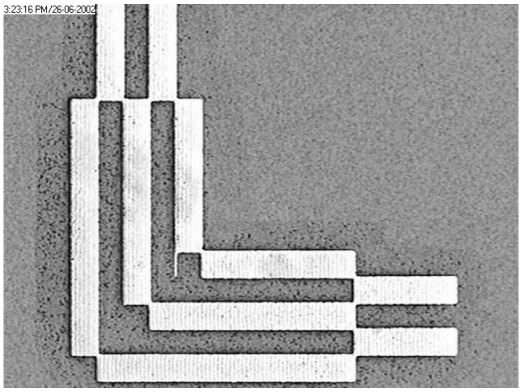

Figure 10. Front-lit & back-lit image of a pattern on the mask with 25 μm wide lines. Vertical raster-scanned lines can be seen in the exposed areas.

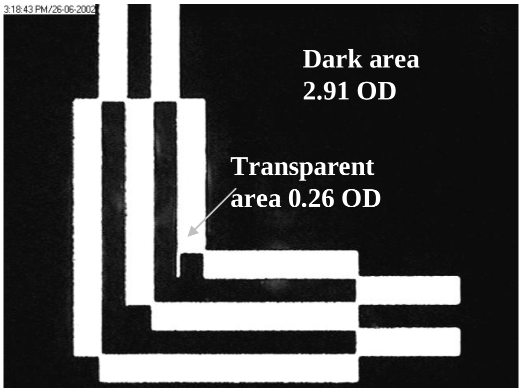

Figure 11. Back-lit image of the same pattern in Figure 10. No raster-scan lines can be seen in the exposed areas. The thinnest line near the center is only 2 μm wide.

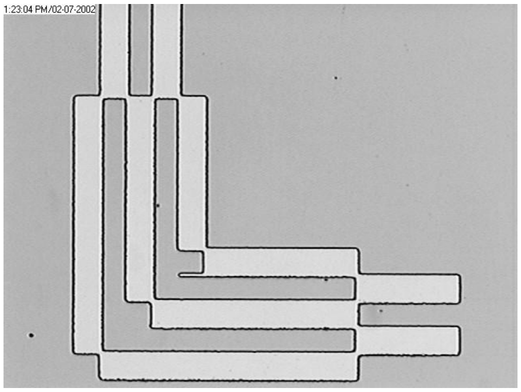

Figure 12. Shipley SPR2FX-1.3 photoresist has been successfully patterned with the same mask. This is the pattern after developed in Shipley MF-319.

to test the direct write photomask, a Quintel 4" mask aligner with a 365 nm Hg source was used to expose a Shipley SPR2FX-1.3 photoresist coated on a chrome film. With a 15 seconds exposure time and a 10 mW/cm$^2$ light intensity, a good pattern was made in the photoresist. These are comparable exposure parameters to those required for processing a chrome mask with the same features. Figure 12 shows the pattern on the Shipley photoresist after developed in developer Shipley MF-319 for 30 seconds.

## 7. MAKING TEST SOLAR CELLS WITH Bi/In DIRECT-WRITE MASK

To better demonstrate the applications of Bi/In film as a thermal resist, a Si anisotropic etching mask material, a direct-write photomask material, and its compatibility with conventional CMOS processes, we have made surface textured solar cells as test devices, as shown in Figure 13.

The first step was to make parallel V-grooves on a silicon wafer. Bi/In resist was deposited on the wafer and laser patterned, followed by a diluted RCA2 solution ($HCl:H_2O_2:H_2O=1:1:48$) development removing the unexposed Bi/In. This developed Bi/In acted as an etch masking process layer on a (100) *n*-type silicon wafer for anisotropic etching in TMAH at 85°C for 30 minutes, followed by standard cleaning and HF dip to strip the Bi/In mask layer. The second step was to create diodes in the V-grooved area. Boron diffusion was carried out after the wet oxidation and oxide definition lithography. Last step was the metallization process. Bi/In was used as the direct-write photomasks for the lithography of the oxidation and metallization layers. The oxide definition mask was created under the same condition as the one reported above. In order to pattern the Al layer a direct write dark field Bi/In mask was used together with a negative photoresist AZ-5214. The process is as following:

- Spin coat 1.4 μm thick AZ-5214 onto the wafer;
- Soft bake at 120°C for 60 seconds;
- Exposure Bi/In mask for 30 second at $P_{365nm} = 10\ mW/cm^2$;
- Hard bake at 120°C for 45 seconds;
- Flood exposure (without mask) for 10 seconds at $P_{365nm} = 10\ mW/cm^2$;
- Developed in MIF for 30 seconds.

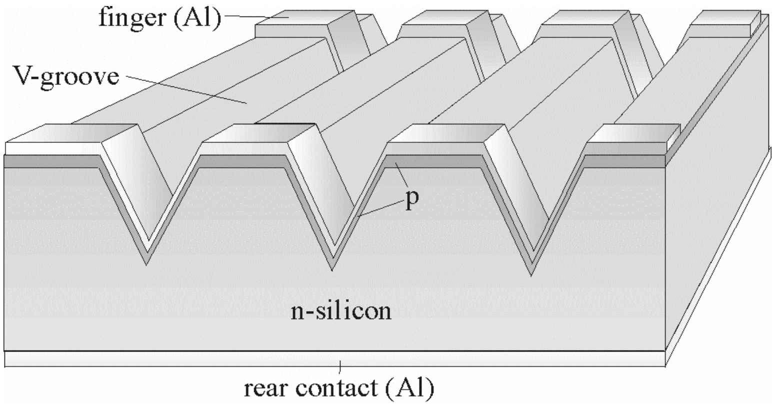

Figure 13. V-groove surface textured solar cells are made on a (100) n-type silicon wafer by using Bi/In as the patterning and masking material.

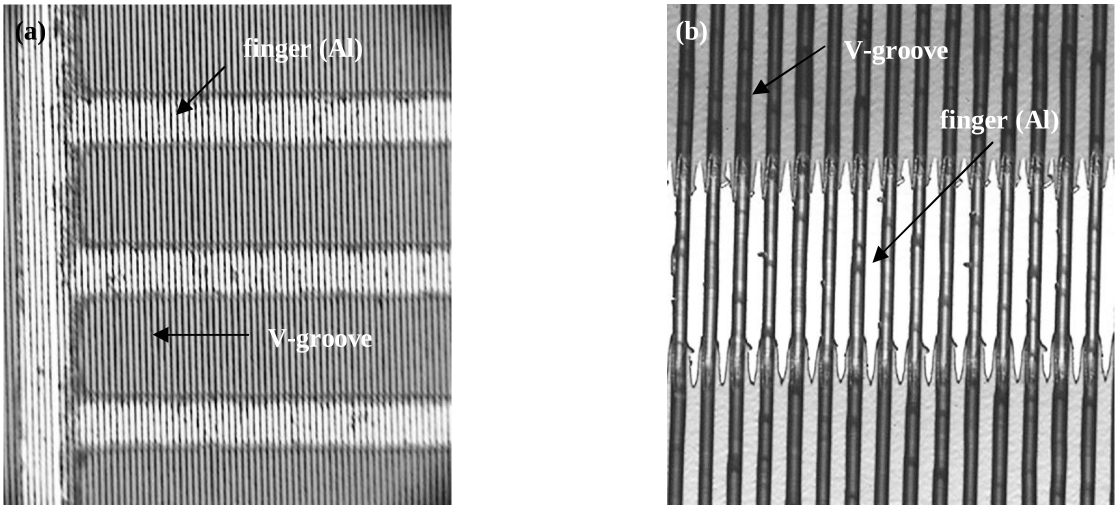

Figure 14. Optical pictures of part of the solar cell. (a) 50× image. The thin vertical lines are the V-grooves. The thick horizontal white lines are Al contacts; (b) 200× image. The V-grooves can be seen.

Table 4. V-groove solar cell electrical performance.

| ***Illumination power (W/m$^2$ at 600nm)*** | **Open Circuit Voltage (mV)** | **Short Circuit Current (mA)** |
|---|---|---|
| 0 | 0 | 0 |
| 9.75 | 135 | 3.8 |
| 19.37 | 280 | 8.1 |
| 40.82 | 320 | 10.4 |
| 87.87 | 352 | 11.2 |

Figure 14 are two optical pictures of part of a solar cell. The vertical fine lines are the V-grooves and the while thick horizontal lines are Al contacts. In order to provide a reference to compare with, normal solar cells were also produced on the other half of the same silicon wafer without being patterned with Bi/In films. Measurement results show that the 1.5 cm$^2$ v-grooved solar cell gives 280 mV open circuit output voltage and 8.1 mA short circuit current under normal florescent tube light at 25°C, which is a fully functioning solar cell. These test results are identical to the reference cells. Table 4 shows the detail of the electrical performance of the cells.

## 8. STRUCTURAL ANALYSIS OF Bi/In FILM

For photomask applications it is important to maximize the Optical Density change, and have the converted minimum OD values extend to the shortest wavelength. Hence it is important to understand the conversion mechanism of Bi/In when exposed to laser. Recent work has shown that the eutectic alloy may be only part of the mechanism.

Profilometry test was carried out on 40 nm thick single Bi, single In layer and 40/40 nm Bi/In bilayer that were DC-sputtered onto silicon substrates. Results show that single Bi film is smooth with Ra = 20 Å, while single In layer is very rough with Ra = 218 Å, as shown in Figure 15. Bi/In, due to the roughness of In is much rougher than Bi, but smoother than In layer, with Ra = 100 Å. The laser scanned Bi/In film gets rougher than the unexposed film, with Ra = 200 Å. Figure 16 shows a profile across the exposed and unexposed area of 40/40 nm Bi/In film (raster-scan laser power = 1.5W with 5× objective lens, scan speed = 1cm/sec, and Y direction increment = 5 μm). Area on the left side of the high peak is laser exposed and that on the right is as-deposited. One can see that the roughness increases after laser exposure and that the exposed area is slightly thicker than the as-deposited area.

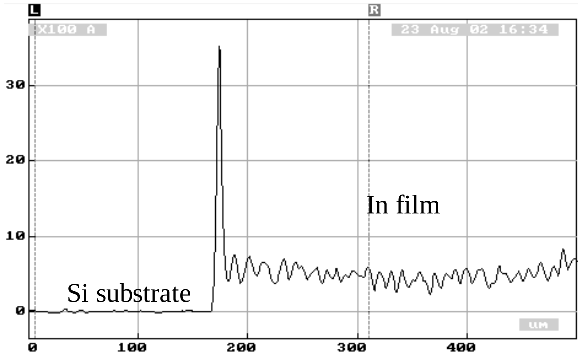

Figure 15. Profilometry result of 40 nm thick, as-deposited, single layer In on silicon substrate. On the left side of the high peak is the Si substrate and the right side is the In film, Ra = 218 Å.

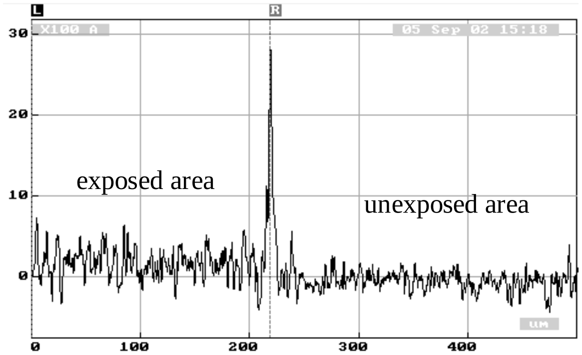

Figure 16. A profile across the exposed and unexposed area of 40/40 nm Bi/In film. Area on the left side of the high peak is exposed, while the right is unexposed.

Recent work by the authors, done in collaboration with Prof. K. Kavanagh at Simon Fraser University and Dr. W. Lennard at University of Western Ontario has explored the structural behavior of the Bi/In films before and after laser exposure[18]. Bi/In films were prepared on different substrates, such as glass slides and silicon wafers. As the laser exposure of Bi/In is a thermal process, furnace annealing of Bi/In films in the air at 150, 200 and 246°C for 3 hours was also carried out in order to compare them with the laser exposed samples. The composition and microstructural characteristics were investigated using profilometry test, atomic force microscopy (AFM), x-ray diffraction $\theta$-$2\theta$ scans (XRD, Cu K$\alpha_1$), Rutherford backscattering spectrometry (RBS) (2 and 3 MeV He$^{++}$), and nuclear reaction analysis (NRA, $^{16}$O(d,p)$^{17}$O).

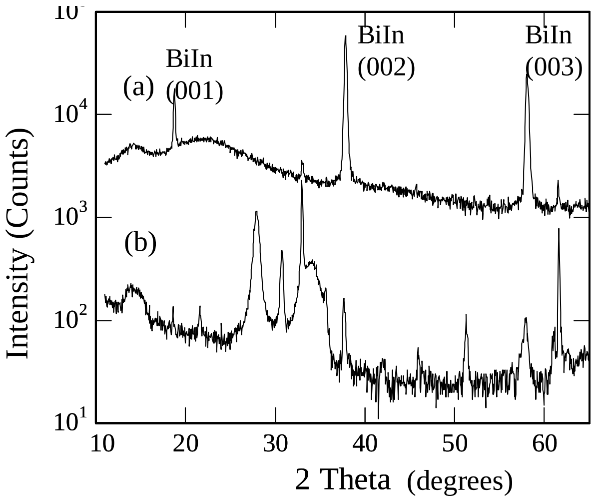

Figure 17. X-ray diffraction θ-2θ scans of BiIn bilayers (45/45 nm) deposited on silicon (a) as-deposited displaced by a factor of 10, and (b) laser exposed in air.

AFM measurements showed that both as-deposited and Argon laser-scanned 12/12 nm Bi/In films are rough (12 nm RMS) with feature sizes of 150 nm. It was noticed that the Bi/In film turned slightly transparent after annealing at 246°C for 3 hours. However it was much less transparent than the laser exposed Bi/In film, indicating a different process than the laser conversion. XRD scans shown in Figure 17 showed the as-deposited films display strong diffraction peaks consistent with BiIn alloy formation. After laser exposure new reflections develop that begin to match some of the known BiIn oxide structures in powder diffraction databases.

RBS spectra and simulation of the data from the as-deposited, furnace annealed at 150°C, 246°C and laser exposed 120/120 nm bilayer films are shown in Figure 18, 19, 20 and 21, respectively. The results for the as-deposited films in Figure 18 clearly show that In is detected on the surface even though it is deposited first, next to the substrate. This is consistent with the severe roughness observed with the profilometry and AFM results of In film. The simulation results showed that the as-deposited film had a 2.5 nm $In_2O_3$ surface layer and a 200 nm thick $Bi_1In_{1.4}O_{0.06}$ film beneath it. It is interesting to notice that after furnace-annealing at 150°C and 246°C for 3 hours, the film structure does not change (as shown in Figure 19 & 20), except that the top $In_2O_3$ layer gets a little thicker, which is 18 and 28 nm, respectively. After laser exposure oxidation of the films was detected as seen in Figure 21. The simulated spectrum was generated by a target film with a 2.5 nm thick surface layer of $In_2O_3$ and a $BiIn_{0.6}O_6$ /$Bi_{0.3}InO_6$ bilayer of average thickness 200 - 245 nm

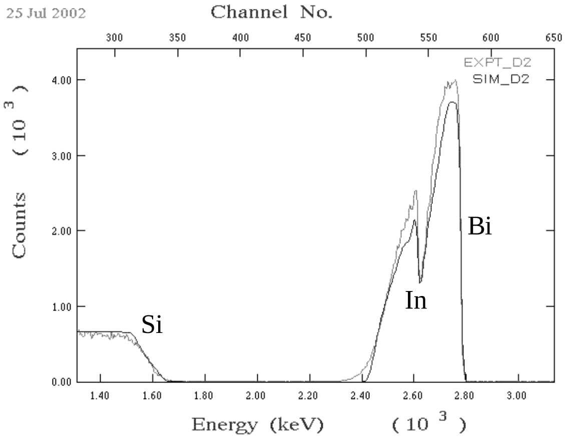

Figure 18. The experiment and simulated RBS spectra of as-deposited 120/120 nm thick Bi/In bilayers on Si.

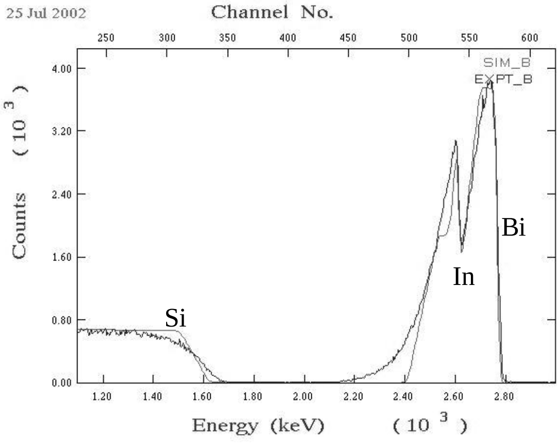

Figure 19. The experiment and simulated RBS spectra of 120/120 nm Bi/In bilayers on Si, furnace–annealed at 150°C.

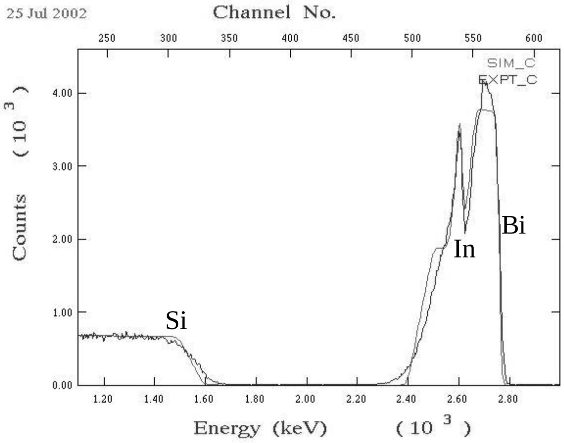

Figure 20. The experiment and simulated RBS spectra of 120/120 nm Bi/In bilayers on Si, furnace–annealed at 246°C.

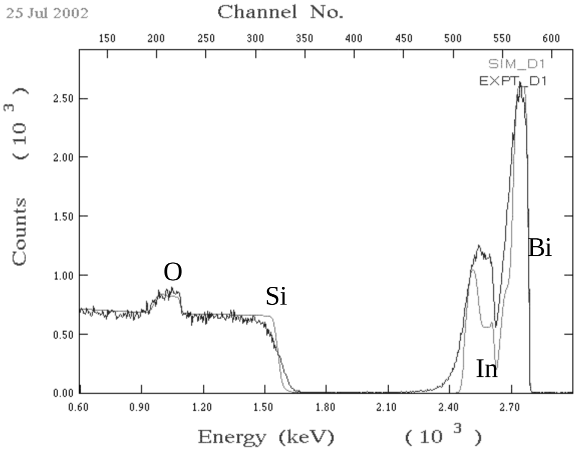

Figure 21. The experiment and simulated RBS spectra of 120/120 nm thick Bi/In bilayers on Si, laser annealed with 0.95 W power and laser beam focused with a 50× objective lens.

below it. Table 5 summarizes the oxygen content obtained from both the NRA and RBS data. There was considerably less oxygen in the furnace-annealed films. Furnace annealing at higher temperature will be conducted in future, as the actual laser exposure temperature could be much higher. It is unknown at this moment whether oxygen is a necessary part of the conversion of Bi/In to a transparent film, as laser exposure tests in a vacuum (50 mTorr) and reducing atmosphere (Nitrogen+10% Hydrogen) showed that the Bi/In films still turned equally transparent after exposure. More stringent vacuum tests will be conducted in future.

Table 5. RBS/NRA results of O concentration.

| ***Sample*** | **[O] NRA ($10^{17}$ at./cm$^2$)** | **[O] RBS ($10^{17}$ at./cm$^2$)** |
|---|---|---|
| as-deposited | 0.22 | 0.27 |
| 150° furnace anneal | 0.87 | 0.84 |
| 200° furnace anneal | 0.80 | 0.70 |
| 250° furnace anneal | 1.5 | 1.3 |
| Laser annealed | 9.5 | 13.5 |

## 9. CONCLUSION

It has been demonstrated that Bi/In bimetallic thermal resist, which turns transparent with high energy laser exposure, can be utilized as a direct-write photomask material for microfabrication applications. With heat treatment at 50 to 90°C before laser exposure, the Optical Density of Bi/In can reach 0.26 at i-line after laser writing, while keeping the unexposed area around 2.91 OD. Working solar cells were successfully made by using Bi/In photomasks together with a standard mask aligner to pattern the oxide and Al layer. XRD and TEM analysis results show that BiIn alloy forms in the as-deposited Bi/In film. RBS and NRA results indicate that the laser conversion of Bi/In could be an oxidation process as large amount of oxygen was found in the laser-exposed Bi/In film. However, it is not known yet whether oxygen is necessary to make Bi/In film transparent. Stringent vacuum test and high temperature furnace annealing test need to be done in future to confirm it.

## 10. ACKNOWLEDGMENT

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