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14. ABSTRACT The primary objective of the STIR project was to investigate the feasibility of realizing graded p-type MgZnO structures, suitable for device integration, using engineered Mg concentration grading. The project was successful in demonstrating a graded Mg _x Zn _{1-x} O epitaxial layer on sapphire, grown by plasma-assisted molecular beam epitaxy (MBE). To realize this accomplishment, MgZnO layers were optimized to allow for up to 46% Mg with no observable phase segregation and sub-nanometer roughness. A primary enabling element of this was the					
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a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			19b. TELEPHONE NUMBER 407-823-6898

Report Title

Final Report: Polarization Induced Doping in p--?ZnMgO (STIR ARO Project)

ABSTRACT

The primary objective of the STIR project was to investigate the feasibility of realizing graded p-type MgZnO structures, suitable for device integration, using engineered Mg concentration grading. The project was successful in demonstrating a graded Mg_xZn_{1-x}O epitaxial layer on sapphire, grown by plasma-assisted molecular beam epitaxy (MBE). To realize this accomplishment, MgZnO layers were optimized to allow for up to 46% Mg with no observable phase segregation and sub-nanometer roughness. A primary enabling element of this was the development of a high temperature ZnO buffer layer, resulting in high Mg concentration with low dislocations. A graded structure with Mg concentration from 0 to 43% Mg was grown and validated with SIMS depth profiling. This work indicates that with proper control over flux sources, a graded MgZnO layer is possible and suitable for polarization doping with the proper background carrier concentration control. Future work should focus on obtaining precise control of the Mg concentration through use of a flux monitor and the potential for using nitrogen to combat background n-type carriers in order to realize a high hole density channel.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received

Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received

Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received

Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received

Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received

Paper

TOTAL:

Number of Manuscripts:

Books

Received

Paper

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	<u>Discipline</u>
Ming Wei	1.00	
FTE Equivalent:	1.00	
Total Number:	1	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):	0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:.....	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

<u>NAME</u>
Total Number:

Names of personnel receiving PHDs

<u>NAME</u>
Dr. Ming Wei
Total Number: 1

Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Technology Transfer

Final Report: Polarization Induced Doping in p-ZnMgO (STIR ARO Project)

Period of Performance: 09/01/2013 – 06/31/2013

Contract Number: W911NF1210485

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Abstract

The primary objective of the STIR project was to investigate the feasibility of realizing graded p-type MgZnO structures, suitable for device integration, using engineered Mg concentration grading. The project was successful in demonstrating a graded $\text{Mg}_{x}\text{Zn}_{1-x}\text{O}$ epitaxial layer on sapphire, grown by plasma-assisted molecular beam epitaxy (MBE). To realize this accomplishment, MgZnO layers were optimized to allow for up to 46% Mg with no observable phase segregation and sub-nanometer roughness. A primary enabling element of this was the development of a high temperature ZnO buffer layer, resulting in high Mg concentration with low dislocations. A graded structure with Mg concentration from 0 to 43% Mg was grown and validated with SIMS depth profiling. This work indicates that with proper control over flux sources, a graded MgZnO layer is possible and suitable for polarization doping with the proper background carrier concentration control. Future work should focus on obtaining precise control of the Mg concentration through use of a flux monitor and the potential for using nitrogen to combat background n-type carriers in order to realize a high hole density channel.

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Scientific Progress and Accomplishments

1. Growth condition was optimized and the Atomic Force Microscope (AFM) images show sub-nanometer roughness for ZnO, with very few density of pits on surface.
2. Wurtzite MgZnO with up to 46% Mg concentration on sapphire was demonstrated without phase segregation. The transmission shows steep absorption edges, indicating homogeneous Mg/Zn+Mg ratio.
3. Good surface morphology for MgZnO with sub-nanometer roughness was achieved by applying a high-temperature ZnO buffer.
4. Gradient structure of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ with x linearly grading from 0% to 43% on sapphire was achieved.
5. Metal-Semiconductor-Metal Schottky photodetectors were fabricated for different Mg compositions. The photodetector based on MgZnO with high Mg composition shows very high responsivity ($\sim 100\text{A/W}$) in the solar blind region and high internal gain, indicating large potential for highly sensitive Ultraviolet detector.

ZnO Growth on Sapphire

High crystal and optical quality ZnO thin films were grown epitaxially on c-plane sapphire substrates by plasma-assisted Molecular Beam Epitaxy. ZnO thin films with high crystalline quality, low defect and dislocation densities, and sub-nanometer surface roughness were achieved by applying a low temperature nucleation layer. The critical growth conditions were investigated to obtain a high quality film: the sequence of Zn and O sources for initial growth of nucleation layer, growth temperatures for both ZnO nucleation and growth layers, and Zn/O ratio. Resultant epitaxial ZnO films demonstrated a root-mean-square surface roughness of 0.373nm for $1\mu\text{m} \times 1\mu\text{m}$ AFM images with clear hexagonal shaped terrace steps, as show in Fig. 1. The x-ray diffraction FWHM for (0002) peak was measured to be 13 arc sec for ZnO, indicating good crystallinity along the growth direction.

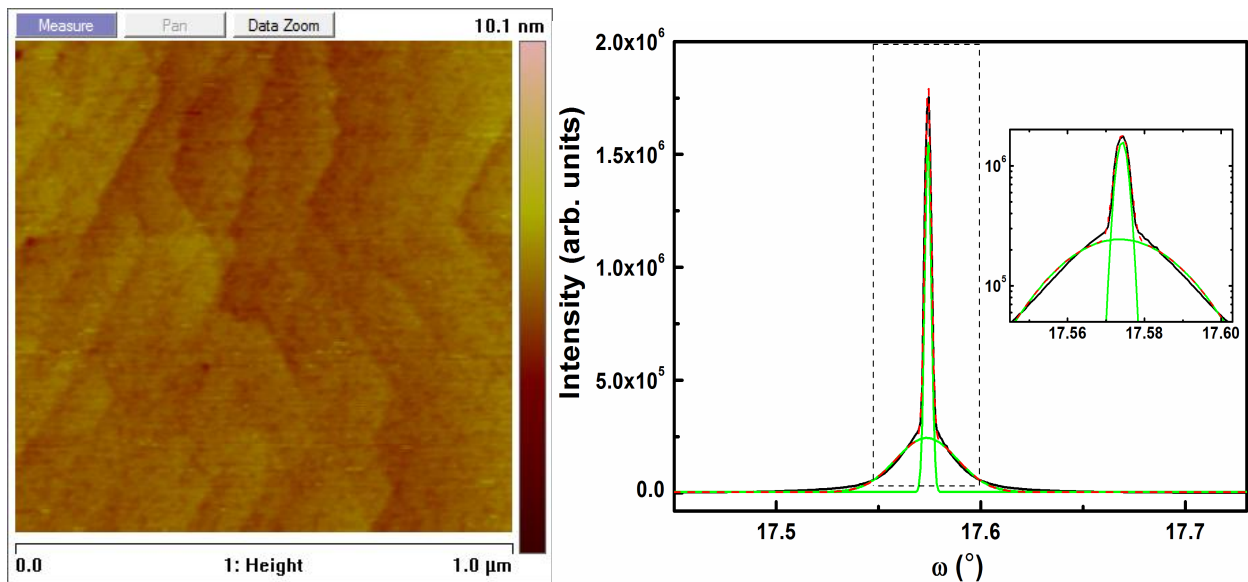


Fig. 1 (Left) AFM images of ZnO with roughness of : 0.384nm for $1\mu\text{m} \times 1\mu\text{m}$. (Right) ω rocking curve of (0002) ZnO epitaxial films grown on sapphire. The inset is the magnified graph in the dashed area.

Wurtzite MgZnO Growth on Sapphire

In Fig. 2 the Cathodoluminescence (CL) spectra of MgZnO layers with up to 46% of Mg are shown together with the results of optical transmission measurements. It can be seen that wurtzite $\text{Mg}_{0.46}\text{Zn}_{0.54}\text{O}$ layers have optical band of approximately 280nm, which is suitable for solar blind application. The transmission shows very steep absorption edge and no other absorption edge was found, indicating no inclusions of cubic phase. This is verified by XRD characterization, which only shows (002) peaks of single crystal wurtzite $\text{Mg}_{0.46}\text{Zn}_{0.54}\text{O}$ epitaxial layers, as shown in Fig. 3. It's also worth note that the grown $\text{Mg}_{0.46}\text{Zn}_{0.54}\text{O}$ layers had very low background concentration of $5 \times 10^{16}/\text{cm}^3$ which is beneficial for p-type doping and the electron motilities of $58 \text{ cm}^2/(\text{V}\cdot\text{s})$. This could be one of the reason that wurtzite MgZnO has a very high internal gain and shows at least four orders magnitude higher of the photoresponsivity than that of cubic MgZnO in the solar blind region.

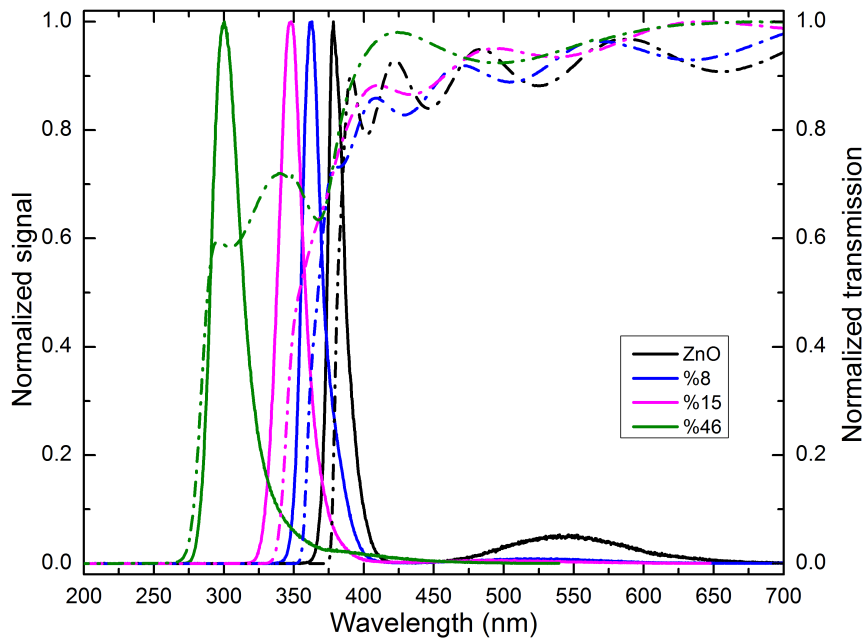


Fig. 2. Room temperature cathodoluminescence (solid lines) and optical transmission (dashed lines) of MgZnO with Mg mole content from 0 to 46%.

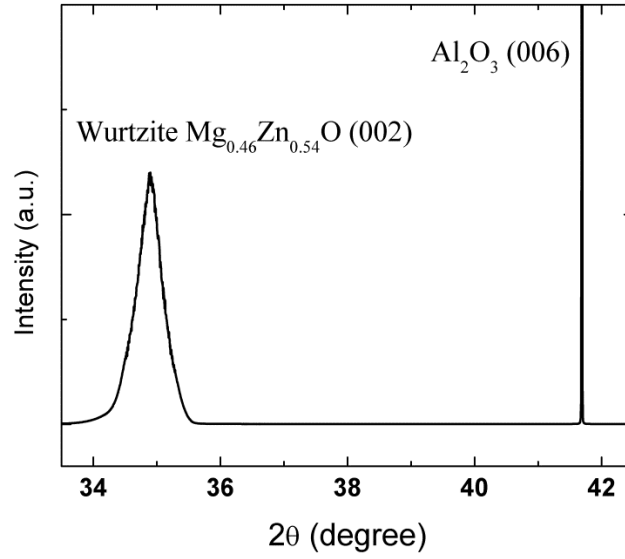


Fig. 3. XRD of (002) peak of Mg_{0.46}Zn_{0.54}O epitaxial layer.

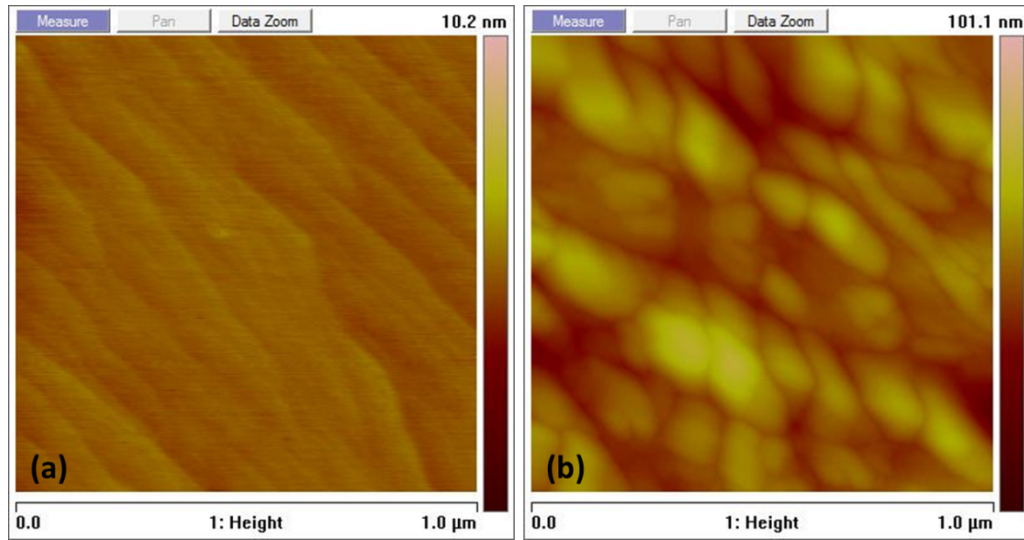


Fig. 4. AFM images of Mg_{0.08}Zn_{0.92}O with (a) and without (b) ZnO high-temperature. The RMS roughness is 0.206 nm (a) and 7.49 nm (b) for 1μm×1μm area.

Although the surface roughness does not influence the performance of photodetectors, a high quality films with good morphology is crucial for light emitters. We optimized the growth conditions for MgZnO and the morphology was found much better if we applied a high-temperature (HT) ZnO buffer layer first. Fig. 4 (b) shows the AFM image for Mg_{0.08}Zn_{0.92}O with only regular low-temperature ZnO nucleation layer, where the surface RMS roughness is 7.49 nm. After applying a 200 nm HT ZnO buffer, as shown in Fig. 4 (a), the surface morphology was significantly improved and the RMS roughness is only 0.206 nm, with clear aligned terrace steps and without any pits on surface.

After calibration of Mg composition in MgZnO, a gradient MgZnO structures were grown. Careful design of the increasing Mg cell temperature was used to achieve a linearly gradient MgZnO structure. Fig. 5 shows the Second Ion Mass Spectroscopy (SIMS) scan of approximately 100 nm thickness of gradient on 100nm ZnO buffer layer. It's shown that the Mg composition was linearly

grading from 0% to 43%. However, no p-type properties were found for these gradient structures by the Hall Effect measurement. Careful investigation shows the polarization effect of MgZnO is much lower than that of AlGaN group, due to the opposite effect of the spontaneous polarization of piezoelectric polarization, as shown in Fig. 6.

For the gradient structure, software called “1D Poisson” was used to calculate the bound charge. The structure for this simulation was a simple PIN ZnO LED with gradient MgZnO as p type layer, as shown in Fig. 7. Both spontaneous polarization [Equation (1)] and piezoelectric polarization [Equation (2)] were considered and the fitted polarization equations are as follows, for the O polar direction:

$$P_{SP} = (0.027x + 0.053)C/m^2 \quad (1)$$

$$P_{PE} = (0.0028229x^2 - 0.020426x + \text{constant})C/m^2 \quad (2)$$

$$P_{total} = (0.0028229x^2 + 0.00657397x + 0.053)C/m^2 \quad (3)$$

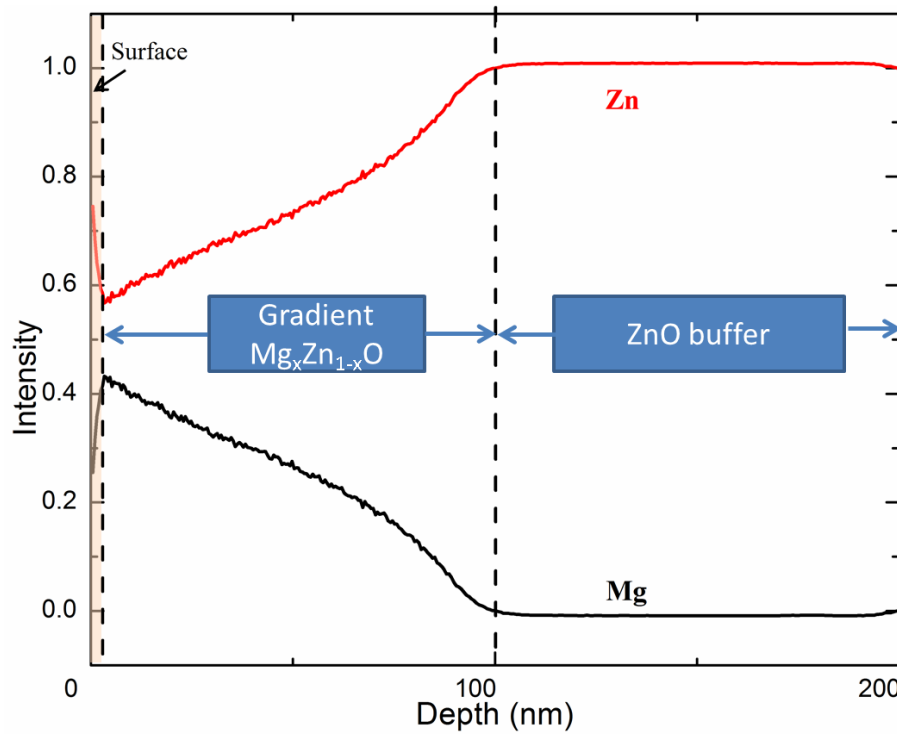


Fig. 5. SIMS scan of gradient $Mg_xZn_{1-x}O$ with x grading from 0 to 0.43.

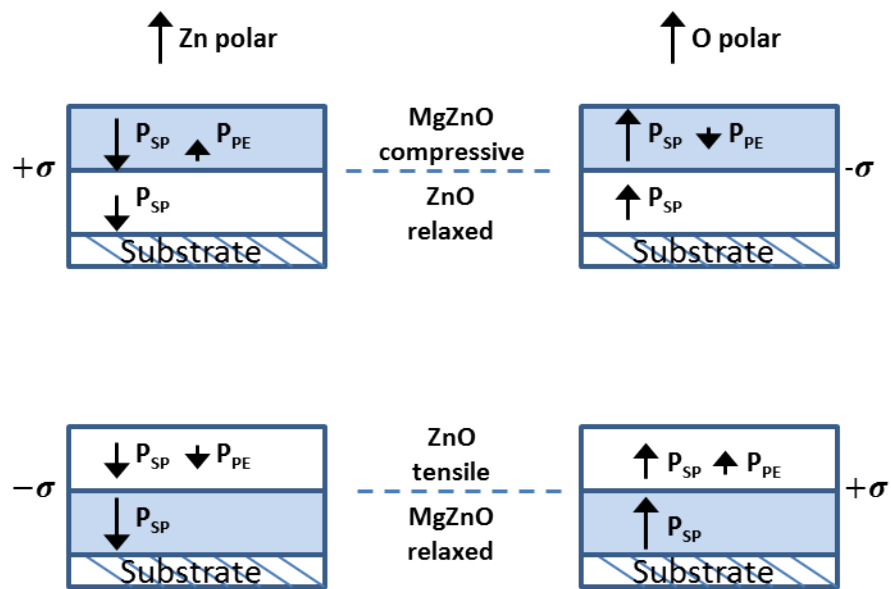


Fig. 6. Bound polarization induced sheet charge with the directions of spontaneous polarization and piezoelectric polarization.

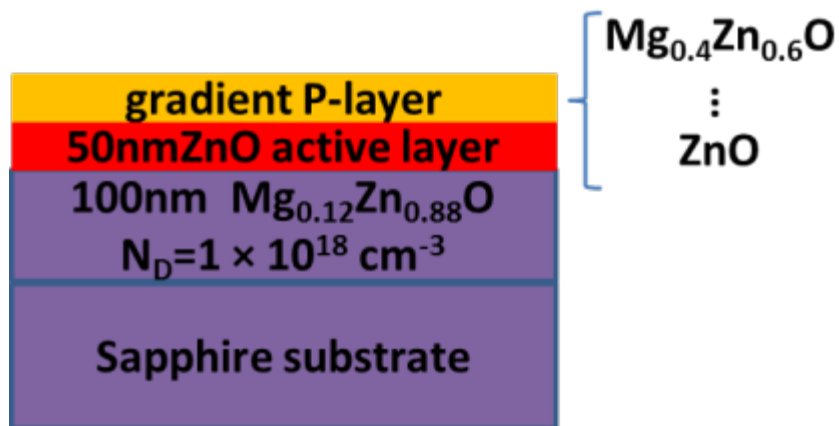


Fig. 7. Structure of PIN ZnO LED with gradient MgZnO as p type layer.

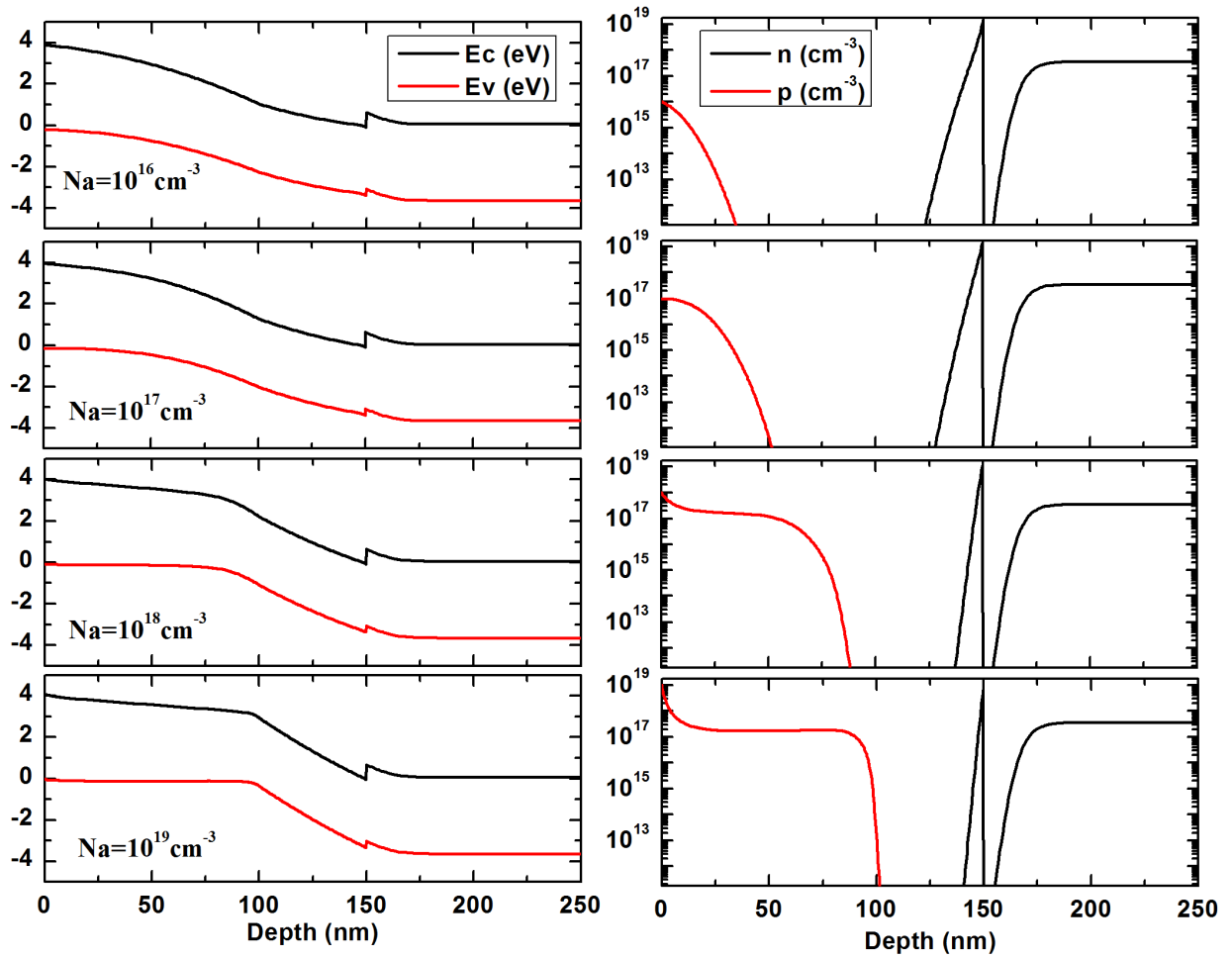


Fig. 8. (Left) Bandgap and (Right) carrier concentrations for Gradient structures with acceptor concentration ranged from 10^{16}cm^{-3} to 10^{19}cm^{-3} . Here the thickness of the gradient structure is 100nm.

Polarization induced doping has been demonstrated recently for both n and p conducting regions, even without introducing impurity dopants. However, as we discussed above, the polarization effect of ZnO is smaller than that of GaN. Here different acceptor concentrations were investigated for p type gradient structures, as shown in Fig. 8. It was observed that holes are compensated if the acceptor concentrations are too low. Therefore, higher acceptor concentration is beneficial for holes distribution in the gradient layer. It's also found that higher acceptor concentration enable the conduction band acts as an electron blocking layer, without blocking any holes.

Wurtzite MgZnO Photodetector

MSM interdigital electrode geometry with Schottky and Ohmic electrodes with interdigital finger spacing ranging from 2 to 15 μm were fabricated from epitaxial layers mentioned above. Below is the photodetectors based on MgZnO alloy with high Mg content that used in solar blind photodetectors, both photovoltaic Schottky and photoconductor. The following is our initial results, we are currently upgrading our UV detection testing system; more accurate results will be achieved till Middle of May.

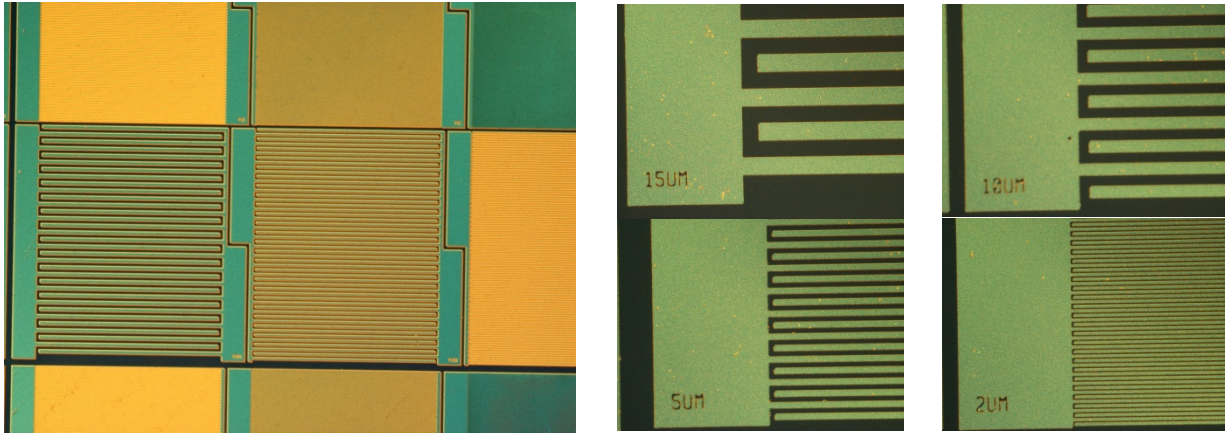


Fig. 9. MSM Geometry photodetectors with Schottky and Ohmic electrodes were fabricated of MgZnO with Mg content from 0 to 46%.

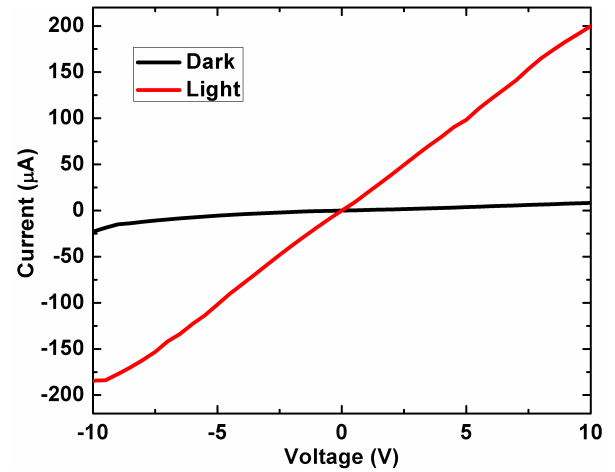
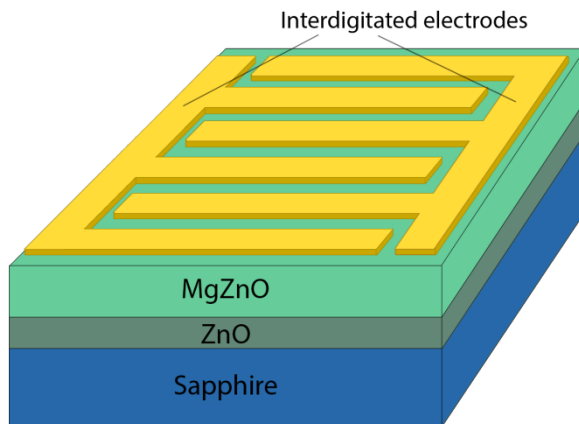


Fig. 10. A 3D cross sectional view of an MSM device with Ni/Au interdigitated electrodes fabricated on $\text{Mg}_{0.46}\text{Zn}_{0.54}\text{O}$ epitaxial layers (Image of the left). Thickness of MgZnO active layer was $0.8\ \mu\text{m}$, ZnO buffer layer was about $0.2\ \mu\text{m}$ thick. I-V characteristics of MSM Photodetectors with $5\ \mu\text{m}$ pitch taken in the dark (black curve, viewgraph on the right) and under light illumination with $\lambda = 300\text{nm}$, $22\ \mu\text{W}$ optical power (red curve, viewgraph on the right).

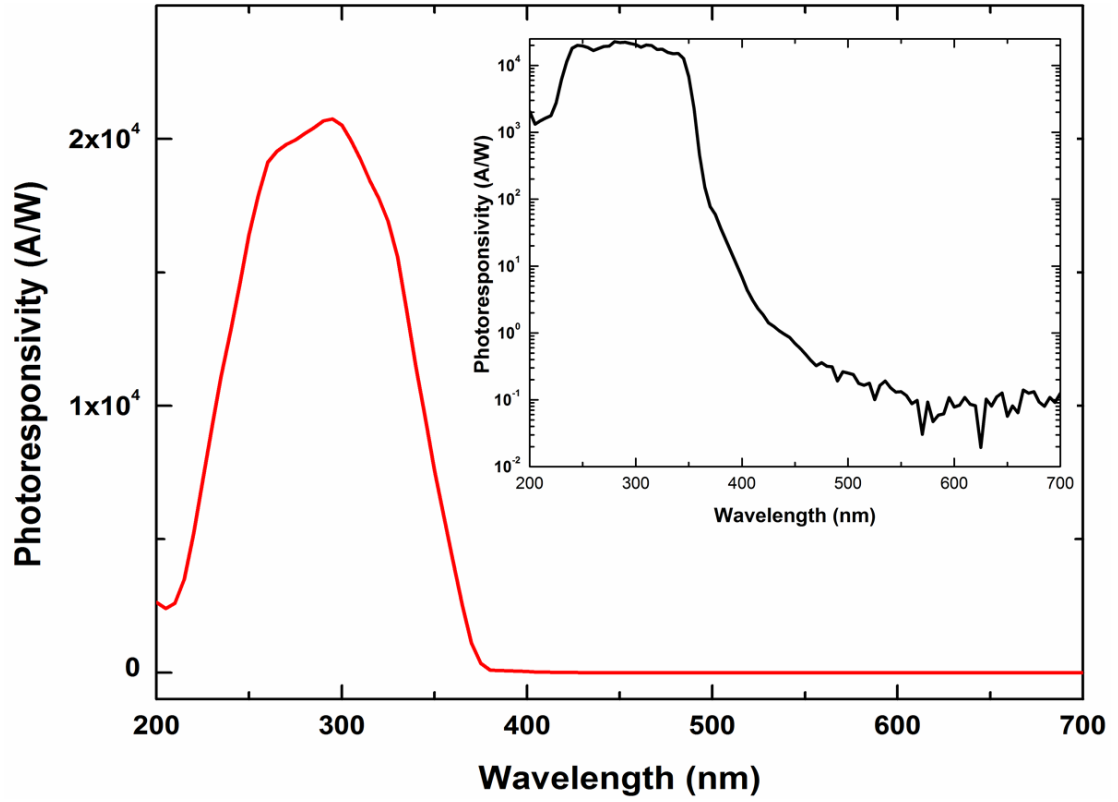


Fig. 11. Responsivity of ZnO MSM photodetector at 5 V bias (the inset is the log scale). The peak Responsivity at 300nm is around 2×10^4 A/W; The rejection ratio of $R_{300\text{nm}}/R_{400\text{nm}}=526$, and $R_{300\text{nm}}/R_{500\text{nm}}=86000$; Dark current is about 750mA. It can be found the cut-off is around 375 nm, where the absorption edge of ZnO is.

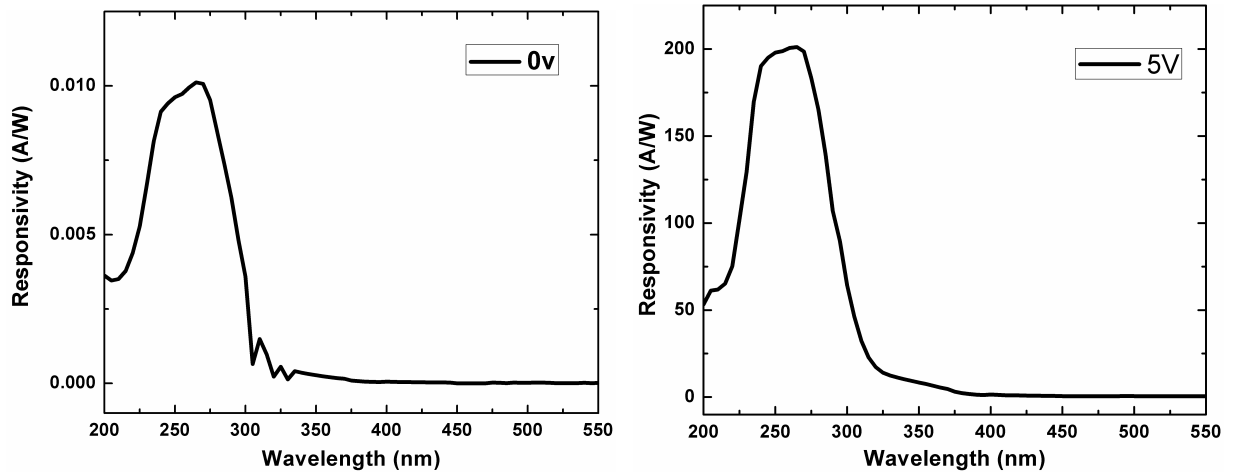


Fig. 12. Responsivity of MSM Schottky photodetector at 0 V bias (viewgraph on the Left) and MSM photconductive detector with 5 V bias (viewgraph on the Right) and measured on the first fabricated single crystal $\text{Mg}_{0.46}\text{Zn}_{0.54}\text{O}$. Absorption and photo carriers generation in the fundamental optical band of hexagonal $\text{Mg}_{0.46}\text{Zn}_{0.54}\text{O}$ alloy contributes to the photocurrent signal.

Schottky photovoltaic devices show responsivity at 265nm of 0.01A/W; dark current of 23pA, rejection ratio $R_{265\text{nm}}/R_{400\text{nm}}=180$ and $R_{265\text{nm}}/R_{500\text{nm}}=505$. Photoconductive devices show

Responsivity at 260nm of 200A/W, resulting in photoconductive gain of 2×10^4 ; dark current at 5V of 2.7 μ A, rejection ratio $R_{265\text{nm}}/R_{400\text{nm}}=140$ and $R_{265\text{nm}}/R_{500\text{nm}}=392$.

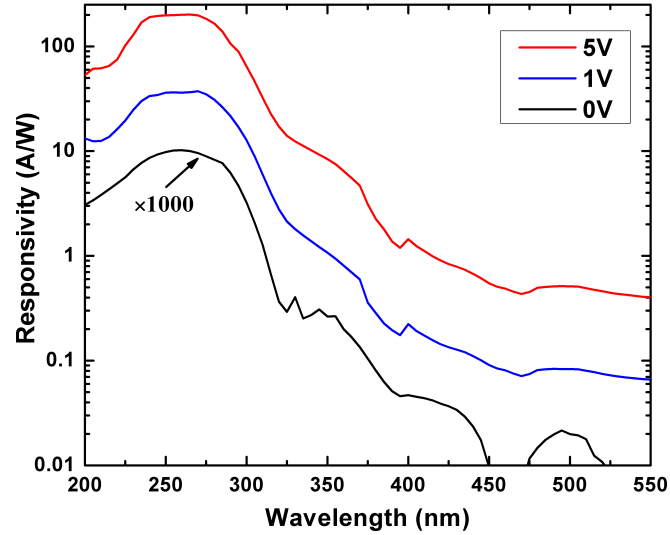


Fig. 13. Log scale plot of the responsivity of a MSM MgZnO photodetector with 5 μ m pitch interdigitated electrodes at biases of 0, 1 and 5 V. The main optical cutoff is in the 280-300 nm range that corresponds to the fundamental optical absorption band in the MgZnO alloy. The small shoulder that appears near 310 - 375 nm is due to the photocurrent contribution from the thin ZnO buffer layer.

Appendix of Accomplishments

1. Publications

None to date.

2. Personnel Metrics

Please complete the below tables, providing the information for this reporting period only. Add rows as needed.

1. Graduate Students

Name	Discipline	Percent Supported
Dr. Ming Wei	Optics & Photonics	100%

2. Post Doctorates

Name	Percent Supported
None	

3. Faculty

Name	National Academy Member	Percent Supported
None		

4. Undergraduate Students

Name	Discipline	Percent Supported
None		

5. Other Staff

Name	Percent Supported
None	

3. Graduating Undergraduate Metrics

Please provide a count for each category below for **Graduating Undergraduates** that were funded by this project and graduated during this reporting period.

Category	Number of Undergraduates
Number who graduated during this period	0
Number who graduated during this period with a degree in science, mathematics, engineering or technology fields	0
Number who graduated during this period and will continue to pursue a graduate of Ph.D. in science, math, engineering, or technology fields	0

Number who achieved a 3.5 GPA to 4.0 (4.0 max scale)	0
Number funded by a DoD Funded Center of Excellence grant for Education, Research and Engineering	0
Number who intend to work for the Department of Defense	0
Number who will receive scholarships or fellowships for further studies in science, math, engineering, or technology fields	0

4. Masters Degrees Awarded

Please complete the following table, adding rows as necessary.

Name	Discipline
None	

5. Ph.Ds Awarded

Please complete the following table, adding rows as necessary.

Name	Discipline
Dr. Ming Wei	Optics & Photonics

6. Technology Transfer

Please provide a listing of any specific interactions or developments which would constitute technology transfer of the research results. Examples include patents, initiation of a start-up company based on research results, interactions with industry/Army R&D Labs or transfer of information which might impact the development of products.

None to report to date.

7. Scientific Progress and Accomplishments

This section should include significant theoretical or experimental advances. Many people use this heading for their technical portion of the report. If you do this, I can put "see attached report" in this box.