1-1-2013

The effect of oxygen flow rate and radio frequency plasma power on cubic ZnMgO ultraviolet sensors grown by plasma-enhanced molecular beam epitaxy

R. Casey Boutwell
University of Central Florida

Ming Wei
University of Central Florida

Winston V. Schoenfeld
University of Central Florida

Find similar works at: <https://stars.library.ucf.edu/facultybib2010>
University of Central Florida Libraries <http://library.ucf.edu>

This Article is brought to you for free and open access by the Faculty Bibliography at STARS. It has been accepted for inclusion in Faculty Bibliography 2010s by an authorized administrator of STARS. For more information, please contact STARS@ucf.edu.

Recommended Citation

Boutwell, R. Casey; Wei, Ming; and Schoenfeld, Winston V., "The effect of oxygen flow rate and radio frequency plasma power on cubic ZnMgO ultraviolet sensors grown by plasma-enhanced molecular beam epitaxy" (2013). *Faculty Bibliography 2010s*. 3730.
<https://stars.library.ucf.edu/facultybib2010/3730>

The effect of oxygen flow rate and radio frequency plasma power on cubic ZnMgO ultraviolet sensors grown by plasma-enhanced molecular beam epitaxy

Cite as: Appl. Phys. Lett. **103**, 031114 (2013); <https://doi.org/10.1063/1.4815995>

Submitted: 05 June 2013 . Accepted: 01 July 2013 . Published Online: 17 July 2013

R. Casey Boutwell, Ming Wei, and Winston V. Schoenfeld

View Online

Export Citation

CrossMark

ARTICLES YOU MAY BE INTERESTED IN

[High-performance solar-blind ultraviolet photodetector based on mixed-phase ZnMgO thin film](#)

Applied Physics Letters **105**, 011117 (2014); <https://doi.org/10.1063/1.4889914>

[Ultraviolet photoconductive detector based on epitaxial \$\text{Mg}_{0.34}\text{Zn}_{0.66}\text{O}\$ thin films](#)

Applied Physics Letters **78**, 2787 (2001); <https://doi.org/10.1063/1.1368378>

[Single-crystalline cubic MgZnO films and their application in deep-ultraviolet optoelectronic devices](#)

Applied Physics Letters **95**, 131113 (2009); <https://doi.org/10.1063/1.3238571>

Applied Physics Reviews
Now accepting original research

2017 Journal
Impact Factor:
12.894

The effect of oxygen flow rate and radio frequency plasma power on cubic ZnMgO ultraviolet sensors grown by plasma-enhanced molecular beam epitaxy

R. Casey Boutwell, Ming Wei, and Winston V. Schoenfeld

CREOL, The College of Optics and Photonics, University of Central Florida, Orlando, Florida 32816-2700, USA

(Received 5 June 2013; accepted 1 July 2013; published online 17 July 2013)

Cubic $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ thin films were produced by Plasma-Enhanced Molecular Beam Epitaxy. Oxygen flow rate and applied Radio-Frequency (RF) plasma power were varied to investigate the impact on film growth and optoelectronic device performance. Solar-blind and visible-blind detectors were fabricated with metal-semiconductor-metal interdigitated Ni/Mg/Au contacts and responsivity is compared under different growth conditions. Increasing oxygen flow rate and RF plasma power increased Zn incorporation in the film, which leads to phase segregation at relatively high Zn/Mg ratio. Responsivity as high as 61 A/W was measured in phase-segregated ZnMgO visible-blind detectors. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4815995>]

ZnO and $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ have attracted much attention due to their oft-cited high excitonic binding energy (60 meV) and ability to tune optical absorption from the near UV (NUV) through the deep UV (DUV).^{1–5} This tuning is accomplished by alloying ZnO ($E_g = 3.37\text{ eV}$) with MgO ($E_g = 7.8\text{ eV}$) and allows for the formation of tunable optoelectronic detectors within that range. It is also well known, however, that the compositional range between ZnO and MgO is interrupted by a crystalline miscibility gap where the wurtzite crystal structure of ZnO is structurally incompatible with the cubic rocksalt structure of MgO.^{6,7} This miscibility gap generally occurs between $x = 0.4$ to 0.6 with some variation between the methods of growth employed.⁸

While a large amount of investigation has been performed on wurtzite $\text{Zn}_{1-x}\text{Mg}_x\text{O}$, significantly less exploration has occurred for its cubic sibling. Cubic $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films produced by a variety of methods have been investigated to understand bandgap evolution and structural stability, but little literature has thoroughly investigated the performance of fabricated optoelectronic devices. In this article, cubic $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ thin films were produced by Plasma-Enhanced Molecular Beam Epitaxy (PE-MBE). Three series of films were grown; two with varying Radio-Frequency (RF) power applied to the oxygen plasma and one with varying oxygen flow rate into the MBE reactor. Interdigitated electrical contacts were fabricated with Ni/Mg/Au and the impact of oxygen growth conditions on device responsivity was investigated.

An SVT Associates oxide MBE was used with thermal Knudsen cells for metal sources and an RF generator was employed for the creation of oxygen plasma. Commercially available (100) MgO substrates were backside coated with 1 μm of titanium for thermal homogeneity of the film during growth. Zinc (6N), magnesium (3N8), and high purity oxygen (6N) were injected into the reactor at a fixed low substrate temperature of 275 °C. Five flow rates were chosen for investigation ranging from 0.5 sccm to 2.5 sccm at a fixed RF power (350 W). Afterwards, six RF powers were applied to the plasma at fixed oxygen flow rate (1.5 sccm) and

ranged from 200 W to 500 W. The produced films were investigated by optical transmission with a Cary 500 UV-Vis Spectrophotometer to determine changes in the absorption edge. Transmission data enabled the calculation of optical bandgap via fitting of a Tauc plot. A Rigaku D-max X-Ray Diffractometer (XRD) utilizing the Cu k-alpha line was used to determine crystalline composition and to identify phase segregation. *In-situ* laser reflectometry determined average hourly growth rate, which was confirmed with standard contact profilometry.

Ni/Mg/Au (30 Å/200 Å/800 Å) Metal-Semiconductor-Metal (MSM) contacts were deposited by thermal evaporation in a BOC Edwards 306 (FL400) metalizer. Contact geometry was 500 μm square with 10 μm finger width and 10 μm spacing. Fabricated devices were illuminated with a Xe lamp (500 W) and a Newport 74125 monochromator collected with a sapphire lens. Spectral responsivity was calculated by dividing the measured photocurrent by incident optical power as $(I_{\text{light}} - I_{\text{dark}})/P_{\text{optical}}$ at each wavelength.

Increasing the oxygen flow rate into the reactor produced a noticeable change in the growth and composition of the film, as shown in Figure 1. Relatively little zinc incorporation was detected by optical transmission at the low flow rate of 0.5 sccm. However, increasing the oxygen flow rate resulted in greater Zn incorporation in the film, redshifting the absorption edge, as shown as dashed lines in Figure 1(a). Increasing oxygen flow rate also had a noticeable impact on the fabricated device responsivity, also shown as solid lines in Figure 1(a). While no photoresponse was detected at the low end of the flow rate investigated, the responsivity gradually increased with increasing flow. It is important to note that most of the devices were tested at 200 V to collect the most distinct signal. However, none of the devices tested which were grown at 2.5 sccm survived testing at 200 V and were instead tested at 100 V to avoid destruction of the contact. Similar 100 V scans on films produced with 1.5 sccm and 2.0 sccm showed approximately half the responsivity intensity as testing at 200 V, suggesting that the responsivity for the 2.5 sccm sample may be twice as intense.

FIG. 1. (a) Increasing flow rate Increased Zn incorporation, as seen in transmission data (dotted lines). This increase is also correlated with an increase in device responsivity (solid lines). (b) Decreasing bandgap (dotted line) is explained by increased Zn incorporation. Increased oxygen flow increases the availability of oxygen atoms on the substrate surface, further increasing growth rate contributed by Zn (solid line).

An increase in Zn incorporation with increasing oxygen flow rate is understood by comparing the ZnO and MgO enthalpies of formation, ΔH . With a ΔH of -601 kJ/mol and -348 kJ/mol for MgO and ZnO, respectively, MgO's formation is much more energetically favorable than that of ZnO.^{9,10} This results in a scenario where mobile Mg on the substrate surface is bonding with much of the available O, leaving the Zn adatoms without suitable bonding sites, i.e., when the surface is Mg-rich and O-poor Zn incorporation efficiency is reduced. As the surface concentration of oxygen increases, the Mg adatoms are satiated and the Zn adatoms are able to bond. The increase in oxygen flow rate also increases the growth rate, seen in Figure 1(b). This is expected from the higher arrival rate of oxygen species to the surface as well as the improved incorporation of Zn in the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ matrix. Figure 1(b) also shows the red-shifting in bandgap as increased Zn incorporation follows from increasing growth rate.

The effect of changing RF power applied to the oxygen plasma is shown in Figure 2. Two different growth series were used to investigate the cubic $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ behavior in this range. The first of these series, shown in Figure 2(a), was grown with an absorption edge near the miscibility gap (measured at ~ 230 nm, 5.4 eV). The second plasma power investigation series, Figure 2(b), was grown with an absorption edge deeper in the UV (measured at ~ 220 nm, 5.6 eV). In the near-gap case, increasing the RF power applied

FIG. 2. (a) In the first plasma series, S1, increasing plasma power eventually led to phase segregation and a dramatic increase in responsivity in the NUV. (b) In the second plasma series, S2, increasing the plasma power with a greater starting concentration of Mg yielded reduced responsivity intensity and did not result in phase segregation.

increased the magnitude of measured responsivity. However, while the response was solar-blind at 300 W, 350 W, and 375 W, phase segregation occurred at 400 W and 500 W. This segregation is understood from crystalline interplay on the surface under growth as competition between wurtzite and cubic rocksalt phases roughens the film.¹¹ This expanded the response region into the NUV and producing sensors that were visible blind. No response was measured for the film produced at 200 W, even with 200 V applied. Visible blind (phase segregated) sensors showed strong photoresponse with only 1 V applied, as compared to the 50 V applied to solar-blind sensors. Phase segregation was confirmed by wurtzite peaks in XRD and a substantial NUV shoulder in the responsivity. While the phase segregated samples did show a broader visible-blind response, the intensity of their response was over three orders of magnitude greater than the single-crystal DUV sensors. A slight increase in Zn incorporation is also seen in Figure 2(a) between the 200W transmission data when compared to the absorption edge of the rest.

In the second power series, all devices were tested at 200 V for greatest signal intensity. Increasing power again resulted in a slight increase in Zn incorporation, evident in transmission data in Figure 2(b). Responsivity, also shown in Figure 2(b), was not detected from the 350 W sample, but rather peaked at 400 W and is steadily reduced with increasing power. This behavior is best understood in Figure 3.

FIG. 3. Increasing plasma power increases Zn incorporation and lowers the bandgap (square points) for both S1 and S2. Responsivity (triangular points) of single crystal films peaked about 375 W. This corresponds with a maximum of the ratio OI/OII in the oxygen plasma composition.

Figure 3 shows the relationship between plasma power, film bandgap, and device responsivity. It appears that increasing plasma power has a very slight effect of increasing Zn incorporation, thereby red-shifting the bandgap (squares). If the bandgap of the film is near the point of crystalline immiscibility, then increasing plasma power was found to increase Zn incorporation to the point of phase segregation, the case of 400 W and 500 W in Plasma Series 1. Phase segregation is avoided, however, if the bandgap is further from the immiscibility edge. As RF power to the plasma is increased, the concentration of atomic oxygen increases. This increase in available atomic oxygen enhances the inclusion of Zn in the growing film, resulting in a slight narrowing of the bandgap.

Figure 3 also shows the responsivity as a function of plasma power for both Series 1 (S1) and Series 2 (S2). This behavior seems more erratic but is rooted in the same physics as the change in Zn inclusion. The major constituents in the oxygen plasma are continually evolving as RF power increases. These active constituents include neutrally charged atomic oxygen (OI), singly ionized atomic oxygen (OII), and singly ionized molecular oxygen (O_2^+ , the dioxygenyl ion). Emission spectra collected from the oxygen plasma indicate that there is a maximum in the ratio of neutral to ionized atomic oxygen (OI/OII) around 350 W, which decreases gradually in both directions. Contrary to nitrogen plasmas, the oxygen plasma source produces less molecular emission at increased power and flow.¹² The responsivity shown in Figure 3 (triangular points) suggests a relationship between maximizing neutral atomic oxygen and increasing photoresponse intensity. Response from S2 is of lower intensity because the bandgap for these films is wider, similar to the device performance seen in Figure 1(a). S1 devices grown at 400 W and 500 W led to phase segregation due to Zn incorporation pushing the composition over the miscibility edge. Transition into the miscibility gap dramatically increased the responsivity magnitude but passed responsivity from solar-blind to visible-blind performance. In Figure 3 phase segregated films, the Zn-rich bandgap is plotted because the wurtzite region dominates absorption in the film.

The devices produced also exhibited a persistent photoconductivity, as shown in Figure 4. This effect was most

FIG. 4. (a) Persistent photoconductivity was not found to vary considerably with increasing oxygen flow rate. (b) Phase segregated samples displayed considerably longer carrier lifetimes than single-crystal films. Neither RF power study indicated a correlation with plasma power.

pronounced for phase segregated films created at high RF power as shown in Figure 4(b), likely due to the increased concentration of deep defects.^{13,14} The effect is also evident to a lesser degree in non-phase-segregated sensors. The concentration of responsible defect(s) does not change relative to responsivity intensity, suggesting that oxygen flow rate and RF power do not affect the charging/discharging. This is evident because increasing oxygen flow rate and plasma power appeared to affect responsivity and charging/discharging times equally. The unaffected behavior is seen in Figures 4(a) and 4(b) where responsivity has been normalized to show no significant change in charging/discharging when varying growth conditions.

Increasing oxygen flow rate and RF plasma power both lead to increased Zn incorporation and red-shifting of the bandgap. This red-shifting is caused by the increase in available atomic oxygen on the substrate surface when increasing either the oxygen flow rate or increasing RF power. These results suggest that the condition for the most intense device responsivity will likely be at a high oxygen flow rate with applied RF power between 375 W and 400 W and an absorption edge near to the miscibility gap. Phase-segregated $Zn_{1-x}Mg_xO$ showed promise for visible-blind detectors and may be explored further by exploiting segregation caused by these two oxygen growth conditions.

The authors would like to thank and acknowledge the U.S. Army Research Office and Dr. Michael Gerhold for financial support under Contract No. W911NF-10-1-0159.

- ¹Y. N. Hou, Z. X. Mei, Z. L. Liu, T. C. Zhang, and X. L. Du, *Appl. Phys. Lett.* **98**, 103506 (2011).
- ²F. D. Aret, S. A. Goodman, M. Hayes, M. J. Legodi, H. A. van Laarhoven, and D. C. Look, *Appl. Phys. Lett.* **79**, 3074 (2001).
- ³J. W. Mares, R. C. Boutwell, A. Scheurer, and W. V. Schoenfeld, *J. Mater. Res.* **25**, 1072 (2010).
- ⁴S. H. Park, *J. Korean Phys. Soc.* **51**, 1404 (2007).
- ⁵M. Wei, R. C. Boutwell, G. A. Garrett, K. Goodman, P. Rotella, M. Wraback, and W. V. Schoenfeld, *J. Alloys Compd.* **552**, 127 (2013).
- ⁶A. Singh, A. Vij, D. Kumar, P. K. Khanna, M. Kumar, S. Gautam, and K. H. Chae, *Semicond. Sci. Technol.* **28**, 025004 (2013).
- ⁷D. Thapa, J. Huso, H. Che, M. Huso, J. L. Morrison, D. Gutierrez, M. G. Norton, and L. Bergman, *Appl. Phys. Lett.* **102**, 191902 (2013).
- ⁸W. Yang, S. S. Hullavarad, B. Nagaraj, I. Takeuchi, R. P. Sharma, T. Venkatesan, R. D. Vispute, and H. Shen, *Appl. Phys. Lett.* **82**, 3424 (2003).
- ⁹D. R. Lide, *CRC Handbook of Chemistry and Physics* (CRC Press, Boca Raton, FL, 2005).
- ¹⁰W. L. Masterson and C. N. Hurley, *Chemistry: Principles and Reactions*, 5th ed. (Thomson Brooks/Cole, Belmont, Ca, 2004).
- ¹¹M. Wei, R. C. Boutwell, J. W. Mares, A. Scheurer, and W. V. Schoenfeld, *Appl. Phys. Lett.* **98**, 261913 (2011).
- ¹²E. Iliopoulos, A. Adikimenakis, E. Dimakis, K. Tsagaraki, G. Konstantinidis, and A. Georgakilas, *J. Cryst. Growth* **278**, 426 (2005).
- ¹³X. Z. Dang, C. D. Wang, E. T. Yu, K. S. Boutros, and J. M. Redwing, *Appl. Phys. Lett.* **72**, 2745 (1998).
- ¹⁴S. Hullavarad, N. Hullavarad, D. Look, and B. Claflin, *Nanoscale Res. Lett.* **4**, 1421 (2009).