Honors Thesis Proposal

For

Assessing the Viability of Sol-gel NiMgO Films for Solar Blind Detection

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Introduction and Motivation

Wide bandgap semiconductors are inherently of central interest for deep-ultraviolet (DUV) technologies.\(^1\) Sufficient advancement in DUV optoelectronics would enable the efficient and affordable realization of UV medical devices, high-density optical data storage, solar blind detection and important water purification technologies.\(^2\) Among the many avenues into the DUV that are being researched, binary and ternary oxides have been among the notable candidates. Successes with ZnO (E\(_g\) = 3.37 eV) based films in particular show tremendous promise for near UV applications and have already been exploited as such.\(^5\) However, to reach increasingly wide bandgap energies, alternative materials with bandgap edges in the 200 – 280 nm spectral region must be investigated.

The wide bandgap material under investigation here is Ni\(_x\)Mg\(_{1-x}\)O. Bandgap tunability in the deep-ultraviolet range has been demonstrated as a function of the nickel concentration, \(x\).\(^5\) The bandgap values that are accessible with this combination range from 3.6-7.8 eV. Epitaxial growth of Ni\(_x\)Mg\(_{1-x}\)O has been demonstrated by our research group, using plasma-assisted molecular beam epitaxy (MBE), and these high quality films have shown responsivity in the DUV range.\(^6\)

Due to the complex nature of the MBE system, the initial cost of the hardware can range between one and five million dollars, not taking into account the other costs associated with operation. This investment can be justified by the potential to yield extremely high quality films, thus presenting the relationship between cost and performance. Oppositely, a sol-gel spin-coating technique presents the opportunity to further investigate the properties of Ni\(_x\)Mg\(_{1-x}\)O and its ability to function as a useful material for solar-blind detectors while requiring relatively inexpensive materials and minimal capital investment. Ultimately, sol-gel Ni\(_x\)Mg\(_{1-x}\)O may prove
to be a lower cost route when compared to previously investigated semiconductors, but the viability and performance of sol-gel synthesized NiMgO remains to be fully investigated.\textsuperscript{7}

**Selected Literature Review**

*Synthesis of Mg\textsubscript{x}Ni\textsubscript{1-x}O thin films with a band-gap in the solar-blind region*\textsuperscript{7}  
Zhenguo Ji, Zuopeng He, Kun Lui, Shichao Zhao, Zhenjie He

This paper, published in the Journal of Crystal Growth, outlines an introductory investigation into a sol-gel technique for producing solar-blind Mg\textsubscript{x}Ni\textsubscript{1-x}O films. Rather than use a spin-coater, the sol is deposited onto the substrate with the use of a dip coater, controlled by a pulse generator and a stepping motor. Next the paper discusses the techniques used to determine the composition, cubic structure, and band-gap of the films. For a sample with Mg\textsubscript{0.3}Ni\textsubscript{0.7}O the theoretical and experimentally calculated band-gap is 4.9 eV. Next a prototype UV detector was used to show that there was a significant response to 254nm UV light, while there was little or no effect when exposed to the sun.

*Deep-ultraviolet photoconductors from epitaxially grown Ni\textsubscript{x}Mg\textsubscript{1-x}O*\textsuperscript{6}  
J. W. Mares, R. C. Boutwell, A. Scheurer, W. V. Schoenfeld

First, some of the solar-blind and DUV applications of Ni\textsubscript{x}Mg\textsubscript{1-x}O are discussed, followed by an explanation of the MBE technique used. After the films were grown using molecular beam epitaxy, they were characterized by several techniques including Rutherford backscattering spectroscopy, x-ray diffraction, and optical transmission measurements. Then, photoconductive DUV detectors were fabricated and also characterized. These devices showed a significant response in the DUV range, with peak responsively at approximately 250 nm.
This book provides a definition of sol-gel as "the preparation of ceramic materials by preparation of a sol, gelation of the sol, and removal of the solvent." These stages are thoroughly described in the chapters of the book, with an emphasis on the science rather than the methods or technology used. Some specific topics of interest include the hydrolysis and condensation of transition metals, aqueous metal salts, the aging process, and sintering.

Methodology

Some preliminary results have been established using the spin-coating technique, and will be discussed in the following section. In this project there are four main topics to be investigated:

1. Growth Optimization

The first area of interest that will be under scrutiny is the actual composition of the film itself and how to demonstrate the bandgap tunability of \( \text{Ni}_x \text{Mg}_{1-x} \text{O} \). This tunability has been proven using MBE growth techniques and we would like to recreate this by varying the concentrations of Ni and Mg in the sol. Specific amounts of nickel acetate and magnesium acetate are dissolved in 2-methoxyethanol and this solution is then spun onto a quartz substrate. Initial results regarding aging the sol, spin-coating speeds, and number of layers will be discussed. Once \( \text{Ni}_x \text{Mg}_{1-x} \text{O} \) films of varying Ni concentrations have been successfully produced, we intend on using a Cary 500 UV-VIS spectrophotometer to gather transmission spectrophotometry data. This information will allow us to calculate the bandgap, and the data points for the different samples should constitute the bandgap range between NiO and MgO. The goals of this effort will be to identify the necessary
synthesis and sintering conditions, synthesize NiMgO films of varying concentration, and to map out the resultant optical bandgaps of the films as a function of concentration.

2. Contact Fabrication/Device Characterization

Once we can create consistent films that exhibit a UV bandgap, the next step will be to optimize the device fabrication process. This can consist of standardizing many different steps in the processing and materials used. We will be producing interdigitated metal-semiconductor-metal (MSM) devices using standard photolithographic techniques. This style of device has been consistently fabricated on MBE grown devices and we will have to assess if any adjustments need to be made for these new films. Next, it will be important to identify which combination of metals will provide good contacts. In the past, Pt/Au (10 nm:150 nm) has been used, but other possible combinations include Ti/Au and Ag/Au. Metals will be deposited on the films using electron beam evaporation (Temescal FC-2000).

3. Photoresponse Testing

The purpose of developing the devices on the films is so we can perform photoresponse testing. This is the stage of the experiment that will ultimately demonstrate the potential for use as ultraviolet detectors. A 300W Xe lamp will provide the source of the UV light. It will be passed through a monochromater and an optical setup will be arranged using UV specified optics to measure the spectral responsivity of the NiMgO films. In order to do so, probe tips placed on the contacts and connected to a Keithley 2400 source meter will measure current and voltage (IV) in the device. Results will be compared between dark and UV illuminated conditions to demonstrate the response to the UV light.
4. Investigate Doping

After the photoresponse has been demonstrated in the UV region there is a potential for further research into doping the Ni$_x$Mg$_{1-x}$O films because NiO is intrinsically p-type and extrinsic doping has been previously demonstrated. While the prior three items are considered requisite for the thesis, doping studies are subject to the progress made on the prior areas and may not be investigated if time limitations ensue. At a minimum, however, the intrinsic electrical properties of the films will be looked at by Hall measurements as a start of assessing their extrinsic doping potential.

**Preliminary Work**

Initial steps have been taken to characterize the growth of the films. Preliminary work/conclusions include:

- Some initial experiments were carried out on glass slides, but we are now using quartz substrates.
- We have been making films of varying Ni concentration. Initial sols consisted of:
  - 0.7g Mg acetate
  - 0.3g Ni acetate
  - 20 ml 2-methoxyethanol

  We have also successfully made sols with the opposite proportion, as well as sols with 50% Ni and Mg acetate.

- When investigating at what rate the samples should be spun, it was determined that speeds near 300 RPM were too slow and the films would crack during drying. After testing various speeds, we have determined that in order to achieve an appropriate thickness, multiple layers are required. Spinning at 2000 RPM for 30 seconds, baking on a 60° C hotplate for 15 minutes, then repeating 5 times, has proven to be an effective way
to create a thick enough film (~550nm) without cracking.

- A common sol-gel technique involves aging the sol. We have investigated aging times ranging from 0-100 hours and determined that approximately 24 hours is a suitable amount of time to age the sol, with times longer than that not displaying significant advantages.

- The most significant results we have obtained thus far are the effects of sintering. Once the film has been created we bake it in a furnace at temperatures between 600-1000° C. Sintering is the process of densification of the sol and in some cases it can increase the quality of the film by further packing the particles together. Figure 1 shows how sintering affected the optical transmission of a Ni_{0.5}Mg_{0.5}O film. The absorption edge is much steeper in the sample that has been sintered, demonstrating a significant increase in the film quality. This graph is also significant because it clearly shows the material is absorbing in the ultraviolet region, a major goal of the project.

![Graph showing optical transmission of a Ni_{0.5}Mg_{0.5}O film before and after sintering at 1000° C.]

FIG. 1. Optical transmission of a Ni_{0.5}Mg_{0.5}O film before and after sintering at 1000° C.
References


