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Nanostructured diamond has unparalleled thermal conduction, hardness, and chemical resistance. It is of interest to industry as a potential coating for Yttrium Orthovanadate ($YVO_4$) crystals used for laser applications, as it would potentially result in high surface thermal conductivity and adhesive-free bonding. The goal of this project was to grow nanostructured diamond thin-films on $YVO_4$ crystals. The development of a LabVIEW interface was required to automate the chemical vapor deposition (CVD) process by which the nanostructured diamond is grown. The LabVIEW interface designed for this project was used to provide temperature information of the laser crystal and to control power shutdown conditions in order to avoid thermal shock to the crystals. Nanostructured diamond film was grown on $YVO_4$ with a microwave plasma chemical vapor deposition (MPCVD) system using a 40-70 torr gas mixture consisting of hydrogen, nitrogen, and methane excited into a plasma ball over the substrate. The growth of the nanostructured diamond was observed in situ using optical thin-film interference of the pyrometer signal used to measure the substrate temperature. The nanostructured diamond films were characterized by Raman spectroscopy and X-ray diffraction (XRD). An interface layer occurs between the sample and thin-film. Further improvements in the nanostructured diamond growth process will be needed for applications of these crystals in high power lasers.
Acknowledgements

Thanks to National Aeronautics and Space Administration (NASA)-Alabama Space Grant Consortium, Research Experiences for Undergraduates (REU) award to UAB, for the support they provided and the opportunity I had to be here.

Thanks to Dr. Yogesh K. Vohra for allowing me to do research in his lab and to Dr. Gopi Samudrala and Jeffery Montgomery for their help in conducting this research and their willingness to train me on the equipment. Thanks also to Jerry Sewell for machining the molybdenum screw and to Dr. Lowell Wenger for assistance with the op-amp circuit design.

Lastly, a special thanks to my family, especially my wife, for their support in going to Alabama for 10 weeks for the REU program.
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Chapter 1

Introduction

1.1 Goals

The goal is to determine a method for successful growth of nanostructured diamond on an Yttrium Orthovanadate ($YVO_4$) substrate. Nanostructured diamond possesses properties that are useful in a wide variety of commercial and academic areas such as quantum devices, lasers, radiation detection, and fusion research [1]. The low cost, hardness, and resistance to wear make nanostructured diamond useful in machining materials for industrial applications.

Laser crystal manufacturers are interested in a method for the deposition of a thin-film, a few nanometers thick, of nanostructured diamond. This would be useful for high surface thermal conductivity, and could potentially achieve adhesive free bonding of $YVO_4$ crystals for use in industrial lasers. Eleven samples of $YVO_4$ were provided by Onyx Optics to conduct these experiments. The method developed to deposit nanostructured diamond onto $YVO_4$ will be adapted from previous efforts on yttrium aluminum garnet (YAG) substrates.

The difficulty in the deposition of diamond on $YVO_4$ is the difference in crystal structure between diamond and $YVO_4$. If the crystal lattice axes do not match between the two materials, then the thin-film may delaminate from the surface of the crystal. The crystal structure of diamond is face center cubic, whereas the crystal structure of $YVO_4$ is tetragonal. The difference between these crystal structures is that the tetragonal structure of $YVO_4$ is the cubic structure stretched along one of its lattice vectors, so they may not align
properly.

1.2 Diamond Thin-films

Diamond is renowned as a material with unmatched physical qualities. In particular, diamond has the highest hardness and thermal conductivity of any bulk material. Those properties determine the major industrial application of diamond in cutting and polishing tools [2] and the scientific applications in diamond knives and diamond anvil cells.

The growth of diamond directly on a substrate allows it to share many of its qualities with other materials. Since diamond has the highest thermal conductivity of any bulk material, layering diamond onto high heat producing electronics (such as optics) allows the diamond to be used as a heat sink [3]. In industry, diamond films are being grown on valve rings, cutting tools, and other objects [2] that benefit from diamond’s hardness and exceedingly low wear rate.

In each case the diamond growth must be carefully done to achieve the necessary lamina-
tion onto the substrate. For this reason, a novel technique for growth on \( YVO_4 \) is necessary. Chemical Vapor Deposition was chosen for the mechanism to create the thin-film for this experiment.

1.3 Chemical Vapor Deposition

Chemical Vapor Deposition (CVD) is a technique for depositing thin-films of materials on wafers or other substrates. To get a desired film, source gases are introduced into a reaction chamber and energy is applied such that the result is the decomposition of the source gas and reaction of the chemicals to form a film. CVD is commonly used to deposit uniform films and augment substrate surfaces. CVD is extremely useful in depositing extremely thin layers of material.

The technique used for these experiments was microwave plasma chemical vapor de-
position. The plasma in the microwave system is detached from all surfaces and in turn no impurities from the reactor materials combine with the source gases during deposition. This
makes microwave plasma methods ideal for high purity commercial applications of diamond films.

CVD growth allows researchers to control the properties of the diamond produced. By regulating the processing parameters, especially the gases introduced, but also the pressure the system is operated under, the temperature of the diamond, and the method of generating plasma, many different materials that can be considered diamond can be made. Single crystal diamond can be made containing various dopants. Polycrystalline diamond (nanodiamond) consisting of grain sizes from several nanometers to several micrometers can be grown \[3\]. These different factors affect the diamond’s hardness, smoothness, conductivity, optical properties and more.
Chapter 2

Methods

2.1 Program

LabVIEW is used to develop measurement systems faster, automate multiple measurements, and make data-driven decisions. LabVIEW is a graphical programming language from National Instruments designed for engineers and scientists to create test, control, and measurement applications. LabVIEW delivers extensive acquisition, analysis, and presentation capabilities in a single environment.

There was a previous LabVIEW program in place, but it was having troubles when switching from manual control to remote control through LabVIEW. When switching to remote control the forward power of the microwave emitter would drop by 400-500 watts. Not only can this be detrimental to any experiment that is being performed, but also can damage the CVD system.

Therefore, a new program was designed to interface with the CVD. This program needed to include calibration functions, graphs and indicators, and subprograms. The calibration functions enable the voltages read to be converted to temperature and power readings, the graphs and indicators show the temperature of the substrate, forward power, and reflected power of the microwave emitter and the subprograms to allow for constant temperature control through the forward power, and linear change of the forward power in a desired amount of time.

The LabVIEW program also needed to include a PID controller. PID stands for
proportional-integral-derivative. A PID controller is a control loop feedback mechanism designed to minimize the error between a process variable and a desired set point. The controller attempts to minimize this error by manipulating a variable. For this system, the manipulated variable is the forward power on the microwave emitter, and the process being controlled is the temperature.

The new program works as intended with all of the required elements, including an easy to understand layout of the block diagram. This program can be easily expanded to control pressure along with forward power. This was not implemented because the correct drivers were not installed to control the pressure, but those drivers do exist, there was just no time due to the limited amount of time left to perform experiments. You can view this program, along with all sub-vis developed for it, in appendix A.

2.2 Electronics

Along with the new LabVIEW program, the data acquisition (DAQ) assistant connections needed to be redone. One of the limitations of the NI USB-6008 DAQ that is being used for this CVD system is that it can only write up to 5 volts, but the CVD system requires 10 volts as an input control. Therefore, a circuit is needed to double the voltage that the DAQ writes to the microwave emitter.

Figure 2.1 is a circuit diagram for the circuit that will be created. This circuit, will double the voltage that is put through it. The equation that governs this relationship is:

\[
\frac{V_f}{V_i} = \frac{R_1 + R_2}{R_1}
\]

When the switch is in the lower position, the circuit will increase the initial voltage by a factor of 2.5.

The previous circuit was on a proto-board designed to prototype circuits, therefore, it was easy to pull out wires or mess it up. In order for the circuit to be permanent it was soldered to a small circuit board and encased in a sturdy, plastic, box. The DAQ assistant was also stored inside the box so the system could not be affected by outside disturbances.
A switch that turns the system from manual to remote control was installed on the top of the box.

### 2.3 Experimental

Prior to growth, the dimensions of each sample were measured to within 10\(\mu\)m. Two of the eleven samples were significantly smaller than the others by about 0.5 mm on both x and y-axes. A special molybdenum screw was then made, with a hole fitted to the maximum dimensions of the nine similar sized samples. This design ensures good thermal contact on the sides and bottom of each sample during growth. The sample initially sat flush with the top of the screw, but later was lowered to about 0.1 mm below the surface of the screw in an attempt to achieve better growth conditions.

In order to grow nanostructured diamond on non-diamond substrates, the substrate must be seeded with nano-sized diamond particles, which will serve as a place for the CVD diamond to grow. For this project, the substrate was seeded by sonication in nanodiamond slurry. The seeded sample is then placed inside the CVD chamber and exposed to microwave induced plasma consisting of hydrogen, nitrogen, and methane directly over the sample at...
Figure 2.2: Circuit Before

Figure 2.3: DAQ Assistant Before

Figure 2.4: Circuit After

Figure 2.5: DAQ Assistant After
low pressure, which allows for the free carbon atoms in the gas to bond and grow on the seeds on the substrate [2]. The mass flow controllers (MFC) control the input of each gas into the chamber. This in turn determines the plasma chemistry.

Before seeding the sample by sonication in nanodiamond slurry, the sample was first cleaned in sonication baths of acetone and then methanol to clean away contaminants. The sample was then placed in the nanodiamond slurry and sonicated for ninety minutes, for an even distribution, to seed the sample. This allows the free carbons created by the plasma to settle onto the seeds in crystalline form. The screw was also cleaned in an acetone bath and sonicated for 30 minutes. The sample was then placed inside the screw and loaded into the CVD chamber, which was then pumped down overnight.

The gas mixture inside the chamber is controlled by the flow rate of the gases: hydrogen, nitrogen, and methane. Initial experiments were performed using mass flow rates of 400, 2.5, 25 sccm (standard cubic centimeters per minute) respectively, but did not result in growth. Nitrogen and methane flow rates were then increased to 3.5 and 35.

To deposit the nanostructured diamond onto the sample, the gases are excited by microwaves creating plasma directly on the surface of the substrate. Changing the pressure inside the chamber, and power given to the microwave emitter, controls temperature inside the chamber. Experiments were done between 40 - 70 torr and 800 - 1000 watts of power given to the microwave emitter.

Film growth is determined by the presence of apparent temperature fluctuations. They are called apparent fluctuations in temperature because the temperature is not really changing. Rather, it appears to be changing due to optical thin-film interference. Thin-film interference occurs when incident light waves that are reflected by the top and bottom layer of the thin-film interfere with each other. This interference creates a new wave, and the pyrometer reads that new wave as the temperature changing. The interference causes a sinusoidal pattern in our temperature readings due to constructive and destructive interference as the film thickness increases. Figure 3.1 shows this idea.

Film thickness and growth rate can be measured by observation of the apparent temperature fluctuations measured by the pyrometer [3]. Growth time can be determined by desired thickness once temperature fluctuations were observed. The temperature fluctuations were
not observed in all experiments. Characterization of the thin-film created on those experiments with observed temperature fluctuations was done using Raman spectroscopy and verified by X-ray diffraction (XRD) crystallography.
Chapter 3

Results

3.1 Experimental Results

Initial experiments were performed to find a chemistry that promoted nanostructured diamond growth on the YV04 samples. Each experiment showed the growth of an interface layer before any nanostructured diamond was grown. It was found after 7 experiments that chamber conditions consisting of 55 torr of pressure inside the chamber and 850 watts of forward power given to the microwave emitter led to good growing conditions seen in situ by apparent temperature fluctuations.

However, nanostructured diamond was not observed on the entire surface of the first sample grown with these conditions, though through Raman spectroscopy portions of the sample showed signs of nanostructured diamond growth. Figure 3.1 shows the apparent temperature fluctuations of Sample 3 recorded by pyrometer. It should be noted that the figures showing the temperature of the substrate in the CVD chamber are actually the potential as a function of time. The potential is the voltage measured by the DAQ controller that is then converted to temperature by the LabVIEW program, but is recorded as potential to the data file. Since this potential is converted to temperature linearly, the data was not changed.

After various other attempts to tweak the growth conditions, a final experiment was done using the same conditions as those done with sample 3. The growth was done for 2 hours to ensure a thick film was grown, with the knowledge that delamination was very
likely. Figure 3.2 shows the apparent temperature fluctuations of sample 11.

Figure 3.1: LabVIEW Data of Sample 3 showing temperature fluctuations. These fluctuations are due to thin-film interference, suggesting film growth.

Figure 3.2: LabVIEW data of Sample 11. Sample 11 was grown under the same conditions as sample 3 for 2 hours to ensure a thick film for characterization.

3.2 Raman Spectroscopy

Raman spectroscopy is a spectroscopic technique used to observe low frequency modes in a system \([6]\). The mechanism is by inelastic scattering, called Raman scattering, of monochromatic light. The laser light interacts with the molecular vibrations of the system, which then change the energy of the laser photons. This change to the energy is usually
a shift up or down and collecting the resulting shifted photons gives us information about the vibrational modes of the system.

Raman spectroscopy is most commonly used in chemistry because the vibrational information of the system is specific to the chemical bonds and symmetry of molecules. This information about the system is essentially a fingerprint by which materials can be identified. Raman spectroscopy was used to verify that there were bonds characteristic to diamond in our thin-film.

The Raman spectrum of diamond is unique because of the chemical bonds. In a Raman spectrum, looking for characteristics of diamond chemical bonds, we look for the Diamond peak at around 1332 cm$^{-1}$, G band (graphite carbon) at around 1550 cm$^{-1}$, and D band (disordered carbon) at around 1345 cm$^{-1}$. All these peaks together are indications of nanostructured diamond [7].

Figure 3.3 shows the Raman spectrum of sample 3. On various other portions of sample 3 no nanostructured diamond was found with Raman spectroscopy. Figure 3.4 shows the Raman spectrum of sample 11. However, to verify the results from the Raman spectrum, XRD measurements were taken of the sample to verify the presence of diamond.

Figure 3.3: Raman spectrum of sample 3. This spectrum was taken on the portion of the sample that growth appeared on. Diamon peak found near around 1332 cm$^{-1}$, G-band at around 1550 cm$^{-1}$ are indications of nanostructured siamond.
Figure 3.4: Raman spectrum of sample 11. This spectrum was taken at the center of the sample.

### 3.3 X-Ray Diffraction Crystallography

X-Ray diffraction (XRD) crystallography is a technique used to identify the crystal structure and molecular composition of a crystal. The mechanism is elastic scattering of an oblique incident beam of finely focused monochromatic x-rays. This elastic scattering produces a diffraction pattern. By changing the incident angle of x-rays and collecting the different diffraction patterns we can analyze the diffraction pattern information to produce information about the density of electron within the crystal and therefore give information about the crystal’s chemical bonds.

Because x-rays have a large penetration depth into any matter, this causes a weak signal for any thin-film. To overcome this weak signal we need to use a glancing angle for our analysis on thin-films. Using a glancing angle for the incident x-ray maximizes the signal coming from the thin layers because most of the x-rays will be reflected. In order to improve the signal to background ratio for the thin-film, a glancing angle of 2° was chosen.

This information is useful to this experiment because it can confirm what Raman spectroscopy has told us about the bonds in our thin-film. We used XRD to look for specific angles of diffraction characteristic to diamond. Those angles are 43.7°, 75.6°, 91.7°, 117.3°, and 141.0° which correspond to different orientations (1 1 1, 2 2 0, 3 1 1, 4 0 0 and 3 3 1 respectively) of the boundary between crystals [2].

Figures 6 and 7 are the XRD scans on sample 11 in two ranges where diamond peaks are expected. Because time had to be scheduled on the machine, and each scan took about 4
hours, we were unable to do a complete continuous scan over the entire range of the desired angles, nor look for more peaks. However, we feel comfortable that the analysis provided by XRD confirms what we found with Raman spectroscopy.

Figure 3.5: XRD scan of sample 11 at the incident angle 2°. The peak at 43.9° corresponds to the 111 diamond diffraction peak[2].

Figure 3.6: XRD scan of sample 11 at the incident angle 2°. The peak at 75.3° corresponds to the 220 diamond diffraction peak[2].
Chapter 4

Conclusions

4.1 Interpretation

Nanostructured diamond has been successfully grown on YV04. In all cases of successful growth an interface layer was present. It was visibly obvious that full, or partial, delamination of the film occurred while ending the experiment, cooling the substrate.

On all samples it was apparent, from the Raman spectrum, an interface layer was being grown on the surface of the substrate, and then the nanodiamond was grown on top of the interface. This interface layer was not optically transparent. More work must be done to identify the interface layer that occurs between the substrate and the thin-film. It appears to be amorphous carbon from initial Raman spectrum analysis. XRD should be used to verify.

Partial delamination of the film may be caused by thermal shock due to the limits of the CVD system. However, there is an operational necessity, for this system, of lowering the forward power from 400 watts to 0 watts in a very short amount of time. This is because of a big spike in reflected power in the microwave wave guide. This can damage or ruin the CVD system completely.
4.2 Future Work

With analysis of the interface layer, it can be determined if it can be avoided. An interface layer may be caused by the mismatch of the crystal structures of $YVO_4$ and diamond. Future work can include research on how to match the axes of the crystal structures, and if a match can be found, how to induce that through CVD growth of nanodiamond.

Conducting this experiment on a different CVD system that does not have the same cool down limitation could prove useful. Cooling down the sample slower, especially from the 400 W 0 W range, could solve the delamination issue. A method for low temperature growth may also help with thermal shock issues that occur.

Onyx Optics also provided twelve samples of Yttrium Aluminum Garnet (YAG) to perform the same experiment with. This year $YVO_4$ was chosen for experimentation, but previous experiments were done with YAG that showed no interface layer. Those experiments showed promise of deposition with the exception of partial delamination occurring, but no interface layer between the thin-film and the substrate. This may be more promising than delamination combined with an interface layer.

4.3 Applications

There is potential application to this research. Due to the good thermal conductivity of diamond, a diamond thin-film on laser gain material may prove to be a great way to cool industrial lasers. It also has potential for Onyx Optics patented adhesive free bonding between the crystals.

Some applications of lasers require a continuous use, which means that the laser must be pumped with continuous power. However, depending on the type of laser, keeping it continuously active is impossible, while in other types it would require a high level of power. Using a lot of power to keep a laser active is very impractical because it would produce a high amount of heat, and maybe bordering on excessive, which could destroy the laser. Finding new ways to cool lasers will allow continuous, constant output operation of the laser.

Adhesive-Free Bonding (AFB) is a patented technology developed and owned by Onyx
Optics, Inc. Onyx Optics believes that coating the surface of laser gain materials, such as $YVO_4$ or YAG, with a nanodiamond thin-film will help in some way with their AFB between crystals. AFB between crystals was developed to produce strong and optically transparent bonds between both similar and dissimilar crystals and glasses. They claim that AFB is as strong, in most cases, as bulk material [8].
Bibliography


Appendix A

LabVIEW Program