CMOS-MEMRISTOR HYBRID NANOELECTRONICS FOR AES ENCRYPTION

MARCH 2013
FINAL TECHNICAL REPORT

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14. ABSTRACT
Complementary metal oxide-semiconductor (CMOS) compatible nanotechnology was investigated under this effort to advance information technology by leveraging the well-proven vast functionality of the existing industry-standard CMOS integrated circuit manufacturing base. Our in-house facility development focused on establishing a very high resolution photoluminescence measurement system to investigate CMOS compatible nanotechnology memristive devices. The reduced size, increased efficiencies and added functionalities of memristive structures may now become available to existing CMOS technologies.

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The authors are truly indebted to the efforts of William “Tony” Burrus. As a student in the summer of 2012 at AFRL/RITB under the Thurgood Marshall College Fund Program, Tony painstakingly recorded for many hours the data assembled in Appendix B of this report containing the Monochromator Slit Width Sensitivity Characterization.
1.0 SUMMARY

Complementary metal oxide-semiconductor (CMOS) compatible nanotechnology was investigated under this effort to advance information technology by leveraging the well-proven vast functionality of the existing industry-standard CMOS integrated circuit manufacturing base. Maintaining compatibility with the current economical manufacturing processes will enable the new memristive device structures to be advantageously integrated onto the same silicon die with CMOS devices. The reduced size, increased efficiencies and added functionalities of memristive structures may now become available to existing CMOS technologies. The stated goal of this effort was to develop facilities and expertise necessary to evaluate test chips to be delivered by SUNY at Albany Center for Nanoscale Science and Engineering (CNSE) and to collaborate with the CNSE concerning hybrid CMOS/memristor architectures for AES encryption. Our in-house facility development focused on establishing a very high resolution photoluminescence (PL) measurement system to investigate CMOS compatible nanotechnology memristive devices. The resulting PL measurement system features a 2-meter focal length Czerny-Turner monochromator with vacuum-insulated cryogenic temperature control down to ~4.5 Kelvin. Specifically, as a demonstration of the PL system capabilities, CMOS compatible copper oxide memristive substrate films currently being used in on-going in-house memristor research were evaluated. An initial set of photoluminescence measurements of a sample copper oxide substrate were recorded at both room temperature and ~4.5 K over a broad range of wavelengths from 330 nm to 860 nm. These copper oxide PL measurement results are presented and discussed in this report. To demonstrate our in-house expertise development, the extensive system operations and element function descriptions detailed in this report are designed to comprehensively instruct all the steps of actual PL system use. An intended purpose of this report is to be useful both as a quick refresher reference for seasoned PL system operators as well a thorough primer for training novice users.

2.0 INTRODUCTION

This document provides user guidance for operating the AFRL/RITB in-house photoluminescence measurement system. It includes laboratory precautions, laser safety guidance, instructive diagrams, component photographs and descriptions of the PL system’s elements and operating procedures. Measurements that show the exquisite wavelength accuracy and resolution capability of this system and the results of a recent set of temperature dependent measurements of new memristive nanotechnology substrate structures are illustrated and discussed.

A schematic diagram of the complete PL system is illustrated in Figure 1 showing the functional interconnections between system elements. Competent operation of the PL system is nontrivial requiring skillful preparation and orchestration of diverse components and electronic instruments functioning in concert followed by careful procedures to safely shutdown the system. An operator should read and understand this document and the operating manuals for each element of the system for effective use. This document is intended to provide an overview of the system and describe how to successfully perform photoluminescence measurement processes. Optimum use of the PL system may only be approached by repeated measurement practice through familiarity with the effects of varying myriad system measurement parameters.
3.0 METHODS, ASSUMPTIONS, AND PROCEDURES

3.1 Laboratory Precautions and Laser Safety

The laboratory is equipped with a dehumidifier which must be attended to maintain relative humidity levels below 75%. Humidity control is required to preclude damaging electrical currents that may be driven by high voltage applied to the photomultiplier tube (PMT). Condensing water vapor could cause surface conductance inside the thermoelectrically cooled PMT socket. Room lights should be turned off for accurate measurements so flashlights are needed for safely moving around in the dark. The red, "Laser Operating", indicator lamp and "Measurement-in-Progress" indicator lamps mounted above the laboratory door must be manually turned on prior to system operation. A door-activated laser interlock shutter blocks the laser beam emission when the laboratory door is open. The interlock must be manually reset if a laboratory power outage occurs.

Laser goggles with a minimum optical density of OD +7 at 325 nm must be worn by all personnel working near the operating HeCd laser. If the red indicator lamp above the laboratory door is on, the laser is operating and goggles must be worn inside the laser curtained area. Appropriate goggles are available in the cabinet on the wall outside Nano-Computing and Computational Intelligence Laboratory. All PL System users must have documented laser safety training before operating the system. It is important to draw the laser curtains closed before turning on the HeCd laser to preclude hazardous emanations.

3.2 Photoluminescence Measurement System and Operating Procedures

3.2.1 Basic PL System Element Function Descriptions. Figure 1 schematically illustrates how the entire PL measurement system is functionally configured. See the “Photoluminescence Measurement System Element List” in Appendix A for brief element descriptions and manufacturer model numbers. Figure 2 shows the center of PL measurement system operator monitors and controls. The heart of the measurement system is a 2 meter focal length, high resolution Czerny-Turner monochromator (Figure 3). The basic principle of operation is to excite the electronic states of a test sample from lower energies to higher energies using short wavelength excitation light and then measure a broad spectrum of light emitted from the test sample.

The system’s excitation source is a HeCd laser tuned to a 325 nm wavelength spectral line producing about 40 milli-watts of continuous output power (Figure 4). Refer to the HeCd laser operating instructions for proper laser power supply (Figure 5) power-on and power-off sequences. This wavelength is short enough to give a photo-excitation energy (3.815 eV) which is larger than the electron valence-to-conduction band gap energies of many materials of information research interest. The HeCd laser has many emission wavelength lines including those from He ions and Cd ions that are present in output beam. These wavelengths will Rayleigh scatter to cause interference with a sample’s photoluminescence wavelengths and must be filtered out before the beam photo-excites the test sample. A narrow 325 nm band-pass filter (Figure 6) provides this function. Unfortunately, the 650 nm sub-harmonic of the main 325 nm laser wavelength is not rejected by this band-pass filter. We plan to procure and use a 650 nm notch filter in front of the 325 band-pass filter to eliminate this wavelength.
Figure 1. High Resolution Photoluminescence Measurement System

- Chopper Wheel Controller
- Vacuum Pump System
- Vacuum Line & Valve
- Vacuum Chamber & Cold Finger
- Cryogenic Temperature Controller
- Cryogenic Helium Refrigerator & Coolant Lines
- Sample Mounted on Cold Finger Holder
- Excitation Source HeCd Laser 40 mW @ 325 nm
- Laser Power Supply/Controller
- Gated Photon Counter
- Trigger from Chopper Drive
- 4-Channel Oscilloscope
- PMT Cooler Heatsink Recirculating Refrigerator
- 350 MHz Pre-Amplifier
- PMT Cooler Power Supply -30 Celsius
- PMT High Voltage Supply
- Mechanical Counter
- Manual Knob
- 2 meter Czerny-Turner High Resolution Monochromator 200-860 nm
- 1800 G/mm Grating
- Scattered Light Chopper Wheel
- Entrance Slit
- Entrance Optics
- Grating Angle Stepper Motor
- Stepper Motor Driver
- Trigger to Photon Counter
- Computer Control & Measurement Software
- RS232 Interface
- GPIB Interface
- USB Interface
Figure 2. PL Measurement System Operator Monitors and Controls

Figure 3. PL Measurement System Monochromator
Figure 4. HeCd Laser Excitation Source

Figure 5. HeCd Laser Power Supply/Controller
A PL test sample can be characterized by the wavelengths and intensities of emitted luminescence photons. Some emitted photon wavelengths are associated with the energy levels available for charge carrier capture known as traps. Traps can be created by material impurities, dopants or by the sample’s microstructure such as defects, dislocations and grain boundaries. Photoluminescence emission wavelengths are directly linked to the density distribution of energy states. Higher emission intensities correspond to higher densities of available states at particular energies for charge carriers to fill (be trapped within).

Other emitted photon energies which may be useful for further characterizing memristive materials can be associated with the Raman Effect. The Raman Effect or Raman Scattering results from inelastic scattering of the incident excitation photons from the vibrational phonons in a sample material. Raman interaction is typically very weak, on the order of 1 in $10^7$ incident photons being Raman shifted. Intensity of Raman scattering is very nonlinearly related to the incident wavelength just as Rayleigh scattering is; it varies inversely with wavelength to the $4^{th}$ power. Raman shifted wavelengths are typically very near the wavelength of elastically scattered Rayleigh excitation due to the relatively low energies of lattice vibrations. Raman wavelengths occur as symmetrical pair emissions on either side of the Rayleigh wavelength (with equal energy differences from the Rayleigh energy) known as Stokes and anti-Stokes. Incident photons can shift energy by either giving or taking energy and momentum to or from vibrational phonons yielding the scattered Stokes and anti-Stokes photons, respectively. Typically of very weak intensities, Raman spectra are characteristics of the vibrational nature of chemical bonds and complement infrared spectroscopy in surface chemical analysis. Raman activity is only allowed by particular spatial symmetries and is due to an induced change in a material’s polarizability by
electromagnetic fields. Without a change in polarizability with inter-nuclear displacements there can be no Raman Effect. Many transition metal oxides which are being used in memristive devices have band gap energies which are greater than the HeCd excitation source but are Raman active with relatively strong intensity Raman scattering. Using the monochromator measurement system to analyze Raman scattering may prove to be a useful characterization tool for these large band gap, highly insulating transition metal oxides.

The PL system features a cryogenic vacuum chamber (Figure 7) which can be used to readily cool a test sample from room temperature to very low temperatures near 4.5 Kelvin. Photoluminescence emission peaks can increase and become narrower as thermal broadening is reduced by lower temperature. Narrow peaks give more accurate measures of energy levels. A vacuum system (Figures 8 & 9) equipped with a turbo-molecular pump provides vacuum to pressures below a micro-Torr which are required for adequate cryogenic thermal insulation. A closed-system helium refrigerator (Figures 10 & 11) with a temperature controller (Figure 12) provides heat transfer to cryogenic temperatures reaching down to 4.5 K in about two hours.

![Cryogenic Vacuum Chamber](image_url)

**Figure 7.** Cryogenic Vacuum Chamber
Figure 8. Vacuum System Front Panel

Figure 9. Vacuum System Rear Panel
Figure 10. Helium Refrigerator Compressor Front Panel

Figure 11. Helium Refrigerator Compressor Rear Panel
A rotating chopper wheel is used to gate sample emission light into the monochromator. Gating the input signal using synchronously chopped photon counting allows subtraction of noise from the signal to improve the system signal-to-noise (S/N) ratio. The chopper wheel is integrated into the monochromator entrance optics and is controlled by a chopper wheel driver (Figure 13 & 14) with a user selectable frequency. Chopper frequencies are best chosen as neither harmonics nor sub-harmonics of the U.S. standard 60 Hz power line frequency and if chosen so, will not be phase coherent with any possible 60 Hz generated noise, interference or modulations. These non-harmonic frequencies will likely integrate random noise to near zero and are desirable for driving the chopper wheel. The maximum selectable chopping frequency is 400 Hz. We have chosen to operate around 131 Hz to reduce wheel bearing wear and audible noise present at higher frequencies.
Figure 13. Entrance Optics & Chopper Wheel

Figure 14. Chopper Wheel Controller
The monochromator grating angle selects the center wavelength that emerges at the exit slit into the photomultiplier tube photon detector (Figure 15). A stepper motor driver (Figure 16) is used to adjust the grating angle which can select a center wavelength anywhere from 185 nm to 860 nm with the 1800 grooves/mm holographic grating installed in the monochromator. Other gratings can be installed to achieve several different specifications of center wavelength range and resolution. A grating home position defined at the monochromator’s grating angle mechanical counter (Figure 17) reading of 650.367 counts (corresponding to a wavelength of 433.578 nm) is specified to calibrate the McPherson stepper drive controller/measurement software. Note that the last dial digit on the counter is an implied decimal value. The technique for reaching this position is described below in “Homing the Monochromator”. When the monochromator is in the home position, the wavelength and monochromator’s grating angle mechanical counter are calibrated so the stepper controller/measurement software can maintain accurate center wavelengths as the grating angle is stepped. As configured with an 1800 g/mm grating, the mechanical counter reading corresponds to 3/2 of the center wavelength measured in nanometers, e.g. a reading of 300 mechanical counts gives a 200 nm center wavelength.

**Figure 15. Photomultiplier Tube**
Figure 16. Grating Angle Stepper Motor Driver

Figure 17. Monochromator Grating Angle Mechanical Counter
A sensitive photomultiplier tube is used to detect monochromator exit photons. The PMT must be chilled to -30 C to minimize thermal electron noise output. Cooling is provided by a Peltier-type thermoelectric cooler with a power supply/controller (Figures 15 & 18). A computer RS-232 serial interface with the power supply/controller and a software program are used to control, maintain and display the desired PMT temperature. A refrigerated re-circulator (Figure 19) containing distilled water coolant is used to maintain the thermoelectric cooler heatsink temperature at room temperature.

Figure 18. Photomultiplier Tube Cooler Power Supply/Controller

Figure 19. PMT Cooler Refrigerated Re-circulator
An adjustable high voltage power supply (Figure 20) applied to the PMT accelerates photoelectrons ejected from a low work function photocathode surface into the vacuum tube. Within the PMT a cascade of dynodes, each with a voltage divided portion of the applied voltage, successively multiplies dynode impacting electrons initiated by original photoelectrons ejected from the photocathode. This electron multiplication process can generate a large group of electrons from a single photon which results in a current pulse at the PMT anode output. The supply voltage should be adjusted to change output of the PMT to maintain countable discrete pulses. Excessive photon flux densities can cause the PMT output to be a continuous output current. Higher intensities of incident photons require lower PMT voltages to remain discrete pulse outputs. Exposing a PMT to high intensity light is undesirable and can result in nonlinear electronic response which must be eliminated by keeping the photocathode dark for a period of time. Refer to the PMT specifications and operating instructions.

Figure 20. Photomultiplier High Voltage Power Supply

The PMT output signal is connected to a 350 MHz preamplifier (Figure 21) for voltage amplification and 50 ohm impedance matching. The impedance matched amplifier output is connected to the input of a photon counter. In the synchronous photon counting mode being used, the photon counter receives a time synchronizing trigger pulse from the chopper wheel driver. This timing trigger signal allows the configuration of two gate channels to be separately integrated for counts. One channel (A) integrates counts during the sample emission (shutter open) portion of the chopper wheel period and the other channel (B) integrates in the shutter closed portion.
Any noise that enters channel B can be subtracted from the signal plus noise in channel A to leave only the emission signal. Proper pulse widths and pulse delays for a given chopper frequency must be programmed into the photon counter. A measurement and control software program controls the grating angle stepper motor and reads the integrated counting data from the photon counter (Figure 22). Integrated photon counts are recorded at each stepped center wavelength and stored in data files for plotting and data analysis. The operation of the PL system software controls is described in detail below.

Figure 21. 350 MHz Photomultiplier Preamplifier
Figure 22. Two Channel Gated Photon Counter

Figure 23. Laser Shutter Interlock Controller
If the laboratory door is opened while the laser is operating, an interlock controller (Figure 23) will automatically shut off the output beam and no excitation source will be present for photo-excitation and measurements must be ceased. The shutter will not reopen when the door is reclosed; it must be rearmed by pressing the momentary button switch labeled “ARM”. If power is lost the power switch must be cycled off and on and the ARM enable switch must be on before the interlock can be rearmed.

3.2.2 PL System Physical Layout. The PL measurement system is implemented on two standard optical tables (each 4 feet x 8 feet) bolted together at a right angle. Figures 24 & 25 (below) illustrate the physical layout of the system elements. Figure 24 shows element positions on the steel optical mounting surface (with standard ¼-20 threaded holes on a one inch matrix) and on the laboratory floor or under the table. Figure 25 shows element positions on the Uni-Strut shelf above the optical tables. A power conditioning constant voltage transformer is used for sensitive instrumentation. Interconnecting cables are shown on the functional schematic diagram in Figure 1. The element locations have chosen for convenience or functional need. In particular, the PMT preamplifier has been located on top of the monochromator as close as possible (with the shortest possible cable) from the PMT output to the preamplifier to minimize signal loss and noise.

Figure 24. Optical Table Layout
3.3 System Preparation

3.3.1 Loading and Aligning a Test Sample in the Cryogenic Vacuum Chamber. The PL measurement system must reach a stable operating condition before measurements can commence. If samples need to be cooled below room temperature they will be mounted in the cryogenic vacuum chamber. See the Janis Research cryogenic vacuum chamber manual for instructions on opening the chamber and mounting samples in the cold finger sample holder. The chamber mount allows easy removal of the lower enclosure by simply tilting the mount near the edge of the optical table exposing the cold finger for access. Mounting a small free-standing substrate may require using an adhesive for securing to a sample holder which can be properly mounted on the cold finger. For ease of adherence and removal, rubber cement can be used for this purpose. Even though volatile organics such as rubber cement are not typically recommended for vacuum systems, the cold temperatures and relatively low vacuum required for thermal insulation allow its
use. Be careful to avoid incidental photoluminescence from the sample substrate adhesive by preventing its photoexcitation from the laser beam. Sample excitation and scattered light must be aligned simultaneously by angular and spatial placements. Sample orientation near 45 degrees relative to the vacuum chamber’s quartz windows is convenient for proper alignment. The sample surface must be aligned with the incident HeCd laser excitation through one of the vacuum chamber quartz windows (Figure 7) while the sample’s scattered light must be aligned through another quartz window with the monochromator entrance optics. This is achieved by careful physical placement and angular orientation of the chamber mount. At the top of the chamber mount post, there are height adjusting bolts for fine vertical position adjustments and leveling (Figure 26). The aperture of the monochromator entrance optics has an f-number near f/17. Placing the sample’s scattered light on the central axis of the entrance optics at the focal length (about 8.1 inches from the entrance optics cavity) is crucial to the monochromator light gathering efficiency. It is good practice to direct specular Rayleigh scattered light away from the entrance optics as this will interfere with the isotropically radiated photoluminescence and Raman scattering of measurement interest. The PMT output can be monitored during fine alignment to maximize light gathering.

When the sample is satisfactorily placed and aligned, the vacuum system should be turned on so the chamber will be evacuated. The vacuum system valve and chamber valve should be opened and the chamber purge needle valve should be closed before pumping begins (Figure 26). Review the Janis Research vacuum system manual for proper operating instructions.

Figure 26. Chamber Mounts and Valves
At this point, the Sumitomo helium compressor (Figure 10) and LakeShore temperature controller (Figure 12) can be turned on to begin sample cooling. Refer to the respective manuals for proper operating instructions. When the vacuum pressure is below the 10 microTorr range, thermal insulation becomes very good. It normally takes more than two hours for the chamber pressure and temperature to reach stable operating conditions in the cryogenic temperature region. The heat capacity of the system decreases with temperature resulting in a nonlinear time-temperature drop. The lower the temperature, the faster the temperature falls until the lowest point is reached near the base temperature of about 4.5 Kelvin. It is very good vacuum system operating practice to close the system valve before shutting down the vacuum system when measurements are completed. This keeps the vacuum system clean and closer to operating vacuum if more measurements on the same sample are planned. If the sample is to be removed, the purging valve should be slowly opened for the vacuum chamber to return to atmospheric pressure before opening. A source of dry air or nitrogen should be used to purge the chamber if the cold finger has not returned to room temperature as ordinary atmospheric air will cause condensation to frost on the interior surfaces.

The HeCd laser power supply (Figure 5) is turned on by a warm-up sequence (see the Melles Griot HeCd laser operating manual). The laser will stabilize to a constant output power after about 20 minutes of warm-up. The laser will need to be used for sample alignment and should be turned on prior to the alignment procedure. If no measurements will be performed for more than 30 minutes on a given measurement workday, the HeCd laser should be placed in standby mode to save the supply of cadmium vapor in the laser tube.

The remaining PL system electronic instrumentation can now be turned on for stabilization. The Fisher Scientific Isotemp refrigerated water re-circulator (Figure 19) should be turned on before the Hamamatsu PMT thermoelectric cooler power supply (Figure 18) is turned on to maintain the cooler heatsink at room temperature. Refer to the equipment operating manuals for proper control. To ensure that the PL system is ready for measurements, use the power-on sequence checklist below.

### 3.4 PL Measurement System Software

#### 3.4.1 Photomultiplier Cooler Supply/Controller.

The photomultiplier must be maintained at a temperature of -30 C to minimize PMT output signal noise due to thermal electron multiplication. The Hamamatsu PMT cooler supply is controlled via RS232 serial interface by a LabView executable program whose Desktop icon is labeled “C9143_c9144”. Be sure the Fisher Scientific refrigerated water re-circulator is operating before turning on the Hamamatsu PMT cooler supply to maintain the cooler heatsink temperature at room temp (~21 C). Executing the Hamamatsu LabView code displays a GUI which initially requests a serial port selection (Figure 27).
Use the mouse to select the “COM1” button and select “COM3” from the com list and then the “NEXT” button (Figure 28).

The temperature can be read from the program’s GUI and can also be graphed in real-time by switching on the virtual toggle switch labeled “Graph” on the right side of the display panel (Figure 29). When the PMT reads -30 degrees C, the PMT is ready for use.
3.4.2 Homing the Monochromator. “Homing” the monochromator is required for very high resolution measurements whenever the stepper counter is manually adjusted using the knurled knob (on the exit side of the monochromator) or the software becomes out of sync with the mechanical counter step number and wavelength. The homing process requires an RS-232 link between the measurement computer and the stepper motor controller (McPherson Model 789A-3). The controller must be powered-on and the remote-enable front panel switch must be asserted. A computer terminal program is used to interface with the controller. Serial communication protocol settings are: 9600 baud rate, 8 data bits, No Parity, and XON/XOFF flow control. These settings have been preloaded into the computer’s terminal program PuTTY under the saved name, “PL Stepper Driver”. Select “PL Stepper Driver” from the saved sessions and press the “Load” button and “Open” (Figure 30).
Figure 30. PuTTY Screen 1

Invoke the communication link and reset the stepper controller by pressing the "space-bar" and (enter) keys. The controller will respond with "v2.55" and prompt with "#" to confirm successful communication and reset (Figure 31).
Figure 31. PuTTY Screen 2

Now read the hardware counter number on the monochromator located below and to the left of the exit slit (Figure 17). Remember the implied decimal point before the last digit. If this number is below 642, the stepper controller will need to be increased using the "+ step number (enter)" command. If this number is above 642, the stepper will need to be decreased using the "- step number (enter)" command. The precise number of steps needed to reach 642 counts can be calculated by knowing that 900 steps, produces exactly 0.1 counts. You should be able to hear the stepper motor turning as it steps when these +/- step commands are executed. When the stepper counter reads somewhere between 640 and 642, the stepper mechanical backlash must be removed by using a "+72000 (enter)" command before final homing can be reached. After this command is executed, turn on the homing LED using the "A8 (enter)" command. Now enable fine stepping mode with the "A24 (enter)" command and seek the home position with the fine stepping home find "f1000,0 (enter)" command. Finally, turn off the homing LED with the "A0" command. The monochromator is now in the home position count at 650.367 steps with the grating angle selecting a center wavelength of 433.578 nm. The mechanical step counter reading is 3/2 of the selected wavelength in nanometers. For example, at the short end of the spectrum (with a monochromator grating of 1800 grooves per millimeter), the counter will read 277.50 counts for a wavelength of 185 nm. At the long end of the spectrum, the counter will read 1290 counts for 860 nm.
3.4.3 Summary of Homing Procedure.

1. Stepper motor driver power-on and remote enable
2. Execute terminal program with communication setup "Name"
3. Press "space-bar" and then "enter" keys
4. Get mechanical counter to be near but below 642 counts using "+Count Number (enter)" command if below and "-Count Number (enter)" command if above
5. Execute "+72000 (enter)" command to remove mechanical backlash
6. Execute "A8 (enter)" command to turn on homing LED
7. Execute "A24 (enter)" command to enable fine stepping
8. Execute "f1000.0 (enter)" command to find Home Position
9. Execute "A0 (enter)" command to turn off homing LED
10. Exit terminal program

3.4.4 Executable LabView Stepper Motor Control and Measurement Program. The homed counter value can now be loaded into the measurement software. Execute the McPherson LabView measurement program (“McPher” shortcut icon on the Desktop, Figure 32). Type 650.367 in the counter entry box and press the enter key. The wavelength should now read 433.578 nm and the monochromator is in the home position. The Stanford Research Model SR400 Photon Counter must be initially configured prior for a measurement sequence. Once the Gate, Counter and Acquisition Mode are initialized they remain fixed until changed when this LabView program is re-executed. Please note that it is not possible to simultaneously execute the terminal program PuTTY and the LabView measurement program as they both require the same RS232 serial interface with the stepper motor controller. Thus, in order to “Home” the monochromator with the PuTTY terminal program the LabView measurement program must be terminated and vice-versa. A quirk in the LabView measurement program requires an initial remote addressing of the photon controller before a measurement sequence can execute properly. This is easily achieved by invoking one of the Gate, Counter or Acquisition buttons and then closing the window.
Figure 32. McPherson Spectrometer Control Screen

The Gate button is used to configure the photon counter’s two gates (Channel A and Channel B) relative to the chopper wheel time waveform. The goal is to delay each gate appropriately to be open during the signal-on portion of the waveform for Channel A and during the signal-off portion for Channel B. Each channel is then set to the same time pulse width which is always shorter in time than the signal-on/off halves of the chopper square wave. For example, if the chopper wheel frequency is 131 Hz the time square wave time period is 1/132 sec = ~7.634 ms. Both channel pulse widths have been selected and configured to be about 20% of chopper period, 1.567 ms. This pulse width value gives allows the gates to be centered in the middle of the respective halves signal-on (Ch A) or signal-off (Ch B) of the chopper square wave period. The gate delays must be configured by trial and error due to the system phase error resulting from the unknown time delay of the actual chopped light signal relative to the photon counter input trigger. The unknown time delay is relatively stable and can be adjusted as needed. By using a high intensity emission line from a calibration lamp input signal, we have chosen a Channel A gate delay of 1.693 ms and a Channel B gate delay of 5.510 ms. The delay is adjusted to center the Channel A gate pulse width in the middle of the strong burst of counts. Notice the difference
between the gate delays is equal to half of the chopper period \((5.51 - 1.693 = 3.817 \text{ ms})\). This difference should always be maintained at half of the chopper period. The gate mode sliders should be set to fixed gate width for typical measurement sequences. The trigger level and slope should be set to about 0.3 V with a positive slope. The T register PreSET counts should be set to 400 for a fast integration time. When the T register is used to count integration time, a value of 400 will give a total integration time of \(400/131 = \sim 3.053 \text{ seconds}\) for a chopper frequency of 131 Hz. A value of 2000 will give an integration time of \(2000/131 = \sim 15.26 \text{ seconds}\). The integration time can be chosen to suit the amount of noise which is present in the signal. For low noise (high intensity signal) measurements having higher signal-to-noise ratios (S/N), a smaller integration time can be used to perform a measurement sequence more quickly. When done adjusting entry values in the window, press the close button to save and exit this function (see SR400 Gate Configurations screen, Figure 33).

The Counter button is used to configure the channel inputs and discriminator settings. We have configured both counter inputs to receive from “INPUT 1” with the T select set to “EXT TRIG”. The discriminator levels are set to fixed values of -42 mV for Channel A and -45 mV for Channel B. Note that these two discriminator voltages are unexpectedly not equal; the reason follows. When observed with no optical signal present (monochromator gates closed), there is a slight circuit asymmetry between the two discriminator channels which causes a greater net integration in Channel B. The asymmetry appears to be constant in time and so allows adjusting the discriminator voltage levels to get a net on-average zero difference between the channels to remove the error of the asymmetry. These values are used with two stages of pre-amplification before the photon counter. Each amplification stage gives a 5x voltage multiplication. The amplifier transfer function can help to increase the signal-to-noise ratio by selectively amplifying frequencies associated with the photomultiplier output pulses. With only one stage of amplification, the discriminator values can be decreased to near -10 mV levels. Amplifying signals by more than two stages has produced overloading input voltage levels to the last amplifying stage. Discriminator slopes are set to negative slope corresponding to the negative pulses from the PMT. The T level and slope are set to 0.3 V and positive, respectively. Press the “Close” button to save and exit this function (see SR400 Counter Configurations screen, Figure 34).

The Acquisition button is used to configure the count mode. The number of periods is how many times the integrations will occur for each measurement. We set this to “1” for each measurement. The count mode is typically set to “A-B for T Preset” which gives the difference between the integrated channel counts. Mode “A, B for T Preset” can be selected if the number of noise counts is desired. In this mode the channel A or B select switch in the main program window is active and must be selected. The display mode is set to “Continuous” so counts can be observed being actively integrated as they are counted. Press the “Close” button to save and exit this function (see SR400 Acquisition Configurations screen, Figure 35).
Figure 33. SR400 Gate Configurations Screen

Figure 34. SR400 Counter Configurations Screen
Figure 35. SR400 Acquisition Configurations Screen

Now that the gate and discriminator settings have been specified, the wavelength band and increment step size can be selected. At this point, it is important to review the monochromator slit width characterization table (Appendix B) to correctly set the monochromator entrance and exit slit widths to optimize for measurement speed while maintaining wavelength peak detection. A typical approach to an unknown PL sample is to select a broad band with relatively large wavelength step size using the appropriate entrance and exit slit widths to ensure reliable peak detections. An estimate of the total measurement sequence time can be calculated by knowing the number of individual wavelength points to be measured multiplied by the integration time of each measurement. A reasonable measurement sequence should not take more than two hours due to the system preparation and proper shutdown times. Also, if there is a software or computer problem during the measurement sequence it is better lose a smaller amount of data. When gross wavelength peaks are identified in the unknown PL sample, much higher resolution wavelength step sequences (with the appropriate monochromator slit widths) can be specified over narrower wavelength ranges that contain the detected gross peaks. At this point, the measurement sequence is ready to begin. If the PL sample is properly mounted and photo-excited, the scattered light will be gathered by the monochromator entrance optics. When the sample temperature is stable at the desired point, the PMT voltage having been properly set and the thermoelectric cooler at -30 C, the room lights can be turned off and the measurement sequence can begin by pressing the program “Scan” button. The program will step through the measurement sequence by integrating pulse counts at each center wavelength point specified. The data is saved in the computer RAM as it is acquired and displayed in a graphing window. Upon completion of the
measurement sequence, a window for saving data opens where the user can create folders and name the data file to be stored. The program features a “Spc-Txt” button which can be used to convert data files which are saved in a “.spc”-extension format to an ASCII text format. When measurements have ended, refer to the power-off sequence checklist below.

3.4.5 4-Channel Tektronix Digital Storage Oscilloscope Software. A universal serial bus (USB) interface allows software control of the Tektronix oscilloscope (Figure 36). The 4 channels allow real-time viewing of both photon counter discriminator channels and their associated time gates. This real-time signal observation is an invaluable tool for monitoring the PL system performance and troubleshooting problems. The software allows the user to store sample graphic screen displays as follows. Invoke the Tektronix software icon labeled “OpenChoice Desktop” (see Tektronix OpenChoice Desktop screens, Figures 37-42). Address the oscilloscope with the “Select Instrument” button. Choose the third entry in the list, “USB...” and press “OK” button. When desired the user can capture a freeze frame in real-time with the “Get Screen” button and save to a data file. Example screen saves are shown below with two different time bases. The yellow trace is the optical + noise signal discriminator output associated with the cyan trace showing the active low Channel A-gate. The magenta trace is the noise-only signal discriminator output associated with the green trace showing the active low Channel B-gate. The photon counter will only count pulses that occur during the respective gates times.

![4-Channel Oscilloscope](image)

**Figure 36.** 4-Channel Tektronix Oscilloscope
Figure 37. Tektronix OpenChoice Desktop Screen 1

Figure 38. Tektronix OpenChoice Desktop Screen 2
Figure 39. Tektronix OpenChoice Desktop Screen 3

Figure 40. Tektronix OpenChoice Desktop Screen 4
Figure 41. Tektronix OpenChoice Desktop Screen 5

Figure 42. Tektronix OpenChoice Desktop Screen 6
3.5 Calibrating the Monochromator

The National Institute of Standards and Technology (NIST) website: http://www.nist.gov/pml/data/asd.cfm contains atomic spectral line data which can be used to verify the specifications of the monochromator wavelength and resolution. Various discharge lamps are available in the laboratory to verify the wavelength accuracy across the spectrum. A convenient calibration lamp power supply/holder is available and easy to use for aligning to the monochromator entrance optics. The mercury spectral doublet at 313.3 nm is particularly useful for this purpose near the short end of the monochromator measurement spectrum and was used to verify the accuracy and resolution of the PL system monochromator (see the Hg 313.3 nm doublet measurement results in Monochromator Specification Verification below - Figure 43).

3.6 Selecting Wavelength Range, Appropriate Slit Widths and Integration Time

When a wavelength range is selected, a wavelength step size and integration time should be calculated to give a measurement time which doesn’t exceed about two hours. The measurement integration time can be changed using the number stored in the T register of the SR400 photon counter (see the manual for operating instructions). At the expense of time, longer integration can be used to increase signal-to-noise ratio when signals are very small compared to random noise. The measurement time per data point is calculated by dividing the number stored in the T register by the chopper frequency. The total measurement sequence time is then calculated by dividing the wavelength range by the wavelength step size and then multiplying by the measurement time per data point.

Refer to the Monochromator Characterization Reference Data (Appendix B) when a wavelength step size is determined. This reference data will provide the minimum slit width necessary to preclude missing the detection of an emission wavelength peak for a given wavelength step size in across the monochromator operating wavelength spectrum. This data was compiled from an exhaustive set of measurements using various calibration lamp wavelengths. Larger slit widths than those specified in the reference data can be used at a given wavelength step size to increase sensitivity but with a concomitant loss of wavelength resolution.

3.7 Adjusting Entrance and Exit Slit Widths

Refer to the McPherson monochromator manual for proper operating instructions. Use the fine micrometer knobs at the entrance and exit sides of the monochromator to change the slit widths. Each of the smallest micrometer divisions corresponds to 5 microns of change in slit width. The minimum entrance and exit slit width opening is also 5 microns. When aligning samples to maximize scattered light gathering into the monochromator, increasing the entrance and exit slit widths can hasten the process by allowing more light to pass through the monochromator, thus increasing the number of detectable photons.

3.8 System Electronic Interference and Noise

As received, the PL system was plagued by various inordinate electromagnetic interferences. Even strong calibration lamp spectral measurements were rendered useless due to the excessive radio frequencies (RF) being generated by specific system elements. Upon
investigation, the stepper motor driver was found to be generating RF signals which were radiating from the driver cable as an antenna. These signals were very intense even when the stepper driver was in a non-stepping, holding mode. A solution was found by wrapping the driver cable in anodized aluminum foil acting as an isolating electromagnetic interference (EMI) shield. As the system became more electromagnetically quiet, other sources of interference were identified and isolated. In particular, the thermoelectric cooler power supply generated interfering signals which were coupling into the PMT signal path. An inline filter was designed and inserted into the cooler drive cable in addition to more extensive use of isolating foil wrapped cables. This has achieved very significant improvements to measurement success with only (as yet unidentified) occasional intermittent very intense bursts of interference that totally obscure particular measurement data points. These intermittent disturbances are managed by re-measuring the obscured data.

3.9 PL System Power Sequence Checklists

3.9.1 Power-On Sequence Checklist.

1. Vacuum pump and valve
2. Cryogenic Temperature Controller and Helium Refrigerator
3. HeCd Laser Controller and Power Supply (wait for stable operation and check the initial power)
4. Refrigerated Water Re-circulator and PMT Thermoelectric Temperature Controller
5. Grating Angle Stepper Motor Driver
6. Entrance Signal Chopper Driver
7. PMT Signal Amplifier
8. Photon Counter
9. PMT High Voltage Power Supply

3.9.2 PL System Power-Off Sequence Checklist.

1. PMT High Voltage Power Supply
2. PMT Thermoelectric Temperature Controller
3. HeCd Laser Controller
4. Helium Refrigerator and Cryogenic Temp Controller
5. Vacuum Pump and Valve
6. Grating Angle Stepper Motor Driver
7. Entrance Signal Chopper Driver
8. PMT Signal Amplifier
9. Photon Counter
10. HeCd Laser Power Supply
11. Refrigerated Water Re-circulator
4.0 Results and Discussion

4.1 Monochromator Specification Verification

A mercury discharge lamp was used to verify the accuracy and resolution of the PL measurement system monochromator. The Hg 313.1 nm spectral doublet is often used as a test for monochromator resolution. The graph below shows the Hg doublet measurement results from the system monochromator (Figure 43). Inspecting the graph reveals the monochromator has clearly resolved the two peaks of the Hg doublet and successfully performed to the wavelength accuracy and resolution of the manufacturer’s specifications. The cited McPherson Model 2062 wavelength accuracy is +/- 0.05 nm and resolution is +/- 0.004 nm. Refer to the NIST database for the Hg spectrum data to see the national standard doublet peak values of 313.1555 nm and 313.1844 nm, respectively.

![Hg 3131 Angstrom Doublet](image)

**Figure 43.** Hg 3131 Angstrom Doublet
4.2 Copper Oxide Substrate PL Measurements

Results of initial photoluminescence measurements of a sample of copper oxide substrate material at room temperature and ~4.5 K are shown in the graphs below (Figures 44-48). There is a strong sub-harmonic peak of the 325 nm HeCd laser excitation at 650 nm. This peak has been truncated for scaling clarity. This 650 nm sub-harmonic is present because it is resonant in the HeCd laser and the 325 nm HeCd band-pass filter allows the sub-harmonic wavelength through. There is a notable increase and narrowing of the broad peaks near 400 nm and 530 nm as temperature was decreased from room temperature to ~4.5 K. This is expected as thermal vibrations shift energies and spread the spectral bandwidth. Zooming in near the 650 nm laser sub-harmonic shows a peak at 658 nm which may be a Raman peak. By filtering the 650 nm line from the incident excitation, the true nature of this peak will be determined. There is an interesting small peak near 588 nm (Figure 47) which will be investigated further at higher resolutions to determine if it is an artifact of the system or a real sample emission.

![Copper Oxide Room Temp](image)

**Figure 44.** Room Temperature Copper Oxide
Figure 45. ~4.5K Copper Oxide

Figure 46. Copper Oxide Temperature Dependence
Figure 47. Copper Oxide Near 650 nm

Figure 48. Copper Oxide Near 588 nm
5.0 Conclusion

This effort has resulted in the demonstration of a very accurate, high resolution photoluminescence measurement system. Photoluminescence data from an actual copper oxide nanotechnology structure sample is given as graphic evidence of the system’s use and high level of performance. The detailed descriptions and instructions presented in this report demonstrate the significant expertise that we have achieved in the development and operation of this custom-isolated, very low noise PL measurement system. Our in-house efforts will benefit from using this system to investigate sample nanotechnology structures used in currently developing memristive devices. Other structures being developed and studied for use in new information nanotechnologies will be characterized using this valuable PL measurement system. As new information nanotechnology structures and processes emerge, we can identify photoluminescence characteristics of promising structures to use as fingerprints. These promising structure PL characteristics can be used to monitor structure processes and provide feedback to manufacturers. Other CMOS compatible structures such as the copper oxide substrate discussed herein will continue to be examined in detail with much higher resolution measurements in narrow wavelength bands of interest. We have demonstrated the value of this in-house research asset and our expertise in operating and facilitating its use.
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Appendix A
Photoluminescence System Element List

1. Monochromator: McPherson Model 2062 2-meter Czerny Turner Monochromator configured with 1800 grooves/millimeter holographic grating to give 0.004 nm resolution over 185-860 nm wavelength range (Figure 3)
2. Stepper Motor Driver/Controller: McPherson Model 789A-3 Controller (Figure 16)
3. Cryogenic Vacuum Chamber: Janis Research Co., Inc. Model SHI-4-1 (Figure 7)
4. Vacuum System: Janis Research Co., Inc. Model TP-70-2DR with turbo-molecular and mechanical roughing backing pumps (Figure 8)
5. Helium Compressor: Sumitomo Model CAN-11 (Figure 10)
6. Photo-Excitation Source: Melles-Griot Model 45-MRM-303-120 HeCd Laser (Figure 4)
7. Laser Controller: Melles-Griot Model LC-500 HeCd Laser Controller (Figure 5)
8. Cryogenic Temperature Controller: LakeShore Model 331 Temperature Controller (Figure 12)
9. Chopper Wheel Controller: Stanford Research Systems Model SR540 Chopper Controller (Figure 14)
10. Photomultiplier Output Signal Pre-Amplifier: Stanford Research Systems Model SR445A DC to 350 MHz Amplifier (Figure 21)
11. Photon Counter: Stanford Research Systems Model SR400 Two Channel Gated Photon Counter (Figure 22)
12. Oscilloscope: Tektronix Model TDS 2024C Four Channel Digital Storage Oscilloscope (Figure 36)
13. Refrigerated Water Re-circulator: Fisher Scientific Model Isotemp BOM#196111010001 (Figure 19)
14. Photomultiplier Cooler: Hamamatsu Model 2010-01 PMT Thermoelectric Cooler & PMT Socket (Figure 15)
15. Photomultiplier Cooler Power Supply: Hamamatsu Model C9143-01 Thermoelectric Cooler Supply (Figure 18)
16. Photomultiplier Tube: Hamamatsu Model R3896 Photomultiplier Tube
17. Photomultiplier High Voltage Power Supply: McPherson Model 7640 PMT Supply
Appendix B

Monochromator Slit Width Sensitivity Characterization

Background

Monochromator entrance and exit slit widths must be adjusted properly for effective and efficient use. Light entering the monochromator through the entrance slit is spread out in angle with wavelength by a grating from which a small bandwidth is selected through the exit slit. The sizes of the entrance and exit slits act as narrow band wavelength filters. The bandwidths of these filters are proportional to the slit widths. Narrower slits are narrower wavelength bandwidth filters. An unknown sample can have wavelength emissions at any point over the entire monochromator bandwidth. By initially allowing broad wavelength bandwidths (large slit widths) to pass through the monochromator, a user can find regions where wavelength emissions are present. This is achieved by using large wavelength step increments that can be quickly measured. Once wavelengths emissions are identified, they can be examined in much higher resolutions (using narrow slit widths) over smaller bandwidths to minimize measurement time. Blindly executing a full monochromator spectrum measurement sequence at the highest resolution (280-860 nm at with01 nm resolution for McPherson Model 2062 with 1800 g/mm grating) by using the minimum slit widths (5 microns) on an unknown sample would be inefficient and time prohibitive. The total number of data points required for this resolution over the full bandwidth on our monochromator is 580,000.

Carefully selecting entrance and exit slit widths for a given wavelength step size increment saves measurement time and ensures emission detection. Over a given bandwidth of interest the monochromator is stepped through the bandwidth with a programmable fixed increment of the monochromator center wavelength. At each increment of the center wavelength photons are detected and integrated over a programmed time period. Photon detectors are typically photomultiplier or avalanche photodiodes. In a photon counting mode, the detector output is in the form of electrical pulses which correspond to detected photons. The output pulses are amplified and input into a photon counting instrument. Photon counts are then integrated over a program selectable time period to yield a total photon count at that wavelength and integration time.

When adjusted properly the entrance and exit slit widths will allow maximum sensitivity at a given step size over the bandwidth of interest. This allows the user to perform a sequence of measurements over a bandwidth in a reasonable amount of time while ensuring no loss of sensitivity to characteristic wavelength emissions. When a characteristic wavelength emission is found, the monochromator steps can be reduced to zoom in on the narrower bandwidth of interest and the monochromator slit widths must then be reduced to give optimum resolution. The data summary chart below can be used as a guide to set the slit widths and step increment.
The data collected here consists of an exhaustive set of entrance and exit slit width variations with a step size selected to ensure sensitivity to wavelength emissions. The monochromator system chopper wheel frequency and integration time period were set to convenient values of 131 Hz and 16 seconds respectively for these data. Symmetric entrance/exit slit width characterization was performed at three wavelengths that span the monochromator operating bandwidth (280-860) using selected lines from a mercury (Hg) plasma lamp. Asymmetric entrance/exit slit width characterization was performed at one Hg wavelength line in the operating bandwidth.

Summary Chart

The following chart of recommended wavelength step increment vs entrance/exit slit widths summarizes the findings of this data collection. The chart gives the monochromator user a guide to follow to perform a sequence of measurements across a bandwidth of interest with optimum sensitivity and resolution.

<table>
<thead>
<tr>
<th>Below 450 nm use:</th>
<th>Between 450 and 700 nm use:</th>
<th>Above 700 nm use:</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 um slits with 0.005 nm step</td>
<td>5 um slits with 0.005 nm step</td>
<td>5 um slits with 0.005 nm step</td>
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<td>10 um slits with 0.005 nm step</td>
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<td>35 um slits with 0.005 nm step</td>
<td>30 um slits with 0.005 nm step</td>
<td>30 um slits with 0.005 nm step</td>
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<tr>
<td>45 um slits with 0.005 nm step</td>
<td>35 um slits with 0.005 nm step</td>
<td>35 um slits with 0.01 nm step</td>
</tr>
<tr>
<td>55 um slits with 0.005 nm step</td>
<td>40 um slits with 0.005 nm step</td>
<td>40 um slits with 0.01 nm step</td>
</tr>
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<td>75 um slits with 0.01 nm step</td>
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<tr>
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<td>100 um slits with 0.025 nm step</td>
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<td>200 um slits with 0.01 nm step</td>
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<td>1500 um slits with 0.5 nm step</td>
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<tr>
<td>1500 um slits with 0.2 nm step</td>
<td>1750 um slits with 0.25 nm step</td>
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<td>2500 um slits with 0.2 nm step</td>
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Symmetric Entrance/Exit Slit Widths

Short Wavelength (313 nm) Measurements at 600 V

Short Wavelength (313 nm) Measurements at 550 V

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Long Wavelength (772 nm) Measurements at 550 V

Counts vs. Wavelength (nm)

- 100 um slits w/ .025 nm step
- 125 um slits w/ .025 nm step
- 150 um slits w/ .025 nm step
- 175 um slits w/ .025 nm step
- 200 um slits w/ .025 nm step
- 250 um slits w/ .01 nm step
- 300 um slits w/ .01 nm step

Long Wavelength (772 nm) Measurements at 550 V

Counts vs. Wavelength (nm)

- 350 um slits w/ .01 nm step
- 400 um slits w/ .01 nm step
- 500 um slits w/ .01 nm step
- 750 um slits w/ .01 nm step
- 1000 um slits w/ .01 nm step
- 1500 um slits w/ .01 nm step
- 2000 um slits w/ .01 nm step
- 2500 um slits w/ .01 nm step

Approved for Public Release; Distribution Unlimited.
Asymmetric Entrance/Exit Slit Widths

5 um Entrance Slits at 600 V

Counts

Wavelength (nm)

5 um Entrance Slits at 650 V

Counts

Wavelength (nm)
15 um Entrance Slits at 600 V

15 um Entrance Slits at 650 V
100 um Entrance Slits at 600 V

Counts

Wavelength (nm)

100 um Entrance Slits at 600 V

Counts

Wavelength (nm)
200 um Entrance Slits at 550 V

Counts

Wavelength (nm)

200 um Entrance Slits at 600 V

Counts

Wavelength (nm)
LIST OF SYMBOLS, ABBREVIATIONS, AND ACRONYMS

AES Advanced Encryption Standard
ASCII American Standard Code for Information Interchange
C Celsius (degree of temperature unit)
CMOS Complementary Metal Oxide Semiconductor
CNSE Center for Nanoscale Science and Engineering
EMI Electromagnetic Interference
eV Electron-Volts
GPIB General Purpose Interface Bus
HeCd Helium-Cadmium
K Kelvin (degree of temperature unit)
LED Light Emitting Diode
NIST National Institute of Standards and Technology
OD Optical Density
PL Photoluminescence
PMT Photomultiplier Tube
RAM Random Access Memory
RF Radio Frequencies
S/N Signal-to-Noise Ratio
SUNY State University of New York
USB Universal Serial Bus