Metal Enhanced Fluorescence in CdSe Quantum Dots by Gold Thin Films

A thesis presented to

the faculty of

the College of Arts and Sciences of Ohio University

In partial fulfillment

of the requirements for the degree

Master of Science

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August 2011

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This thesis titled

Metal Enhanced Fluorescence in CdSe Quantum Dots by Gold Thin Films

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Abstract

DESAI DARSHAN B., M.S., August 2011, Physics and Astronomy

Metal Enhanced Fluorescence in CdSe Quantum Dots by Gold Thin Films

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Visible electromagnetic radiation can create excitons in semiconductor quantum dots, and surface plasmons on metal thin films. Hence, when visible electromagnetic radiation interacts with semiconductor quantum dots that are in proximity to metal thin films, the excitons can couple with the plasmons in such a way that may cause enhancement in radiative emission from such semiconductor-metal nanostructures. Study of such exciton-plasmon interactions has the potential to understand and control the energy transfer in such systems at nanoscale. This thesis describes a method to create semiconductor-metal nanostructures by using Electron beam lithography, and provides an evidence of enhanced radiative emission that is suggestive of expected exciton-plasmon coupling.

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Acknowledgments

I would like to thank my research advisor, Dr. Eric Stinaff, for his support and guidance during this research study. I also thank my laboratory partners: Kushal Wijesundara, Swati Ramanathan, Thota Venkata Ramana Kumar, and Nathan Turner for their help and support. I also thank Dr. David Tees for access to Fume hood facility and Spin-coating device, and NQPI for access to Electron beam lithography device. Lastly, I would thank all my friends in department of Physics and Astronomy. It has been a pleasure to know you all...
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Chapter 1: Motivation

This thesis is an attempt to investigate interactions between excitations in semiconductor quantum dots and metal thin films in presence of visible light.

Semiconductor quantum dots are confined in all three spatial directions, and hence their energy band structure is discrete. Their interaction with light causes optical transitions of an electron, creating a quantum-confined electronic state called exciton. Such excited state may relax by radiative emission.

Metal thin films are confined in one spatial direction. Metals have a high free electron density. Hence, when visible light is shone on a metal thin film, these free electrons are expected to coherently oscillate at corresponding optical frequencies. Such collective excitation is known as surface plasmon. The incident light can couple with surface plasmon to create electromagnetic wave on the surface, which is known as surface plasmon polariton. Surface plasmon polaritons can cause concentration of the electromagnetic field energy near the metal surface\(^1\).

When visible light is incident on a system with quantum dots in close proximity to metal thin films, the excited state of quantum dot may couple with the excitations on metal thin film, which may cause enhancement of the radiative emission from such quantum dot-metal thin film nanoscale systems.
A motivation behind the study of such coupling is to understand and control the energy transfer at nanoscale by controlling the properties such as dimensions of the metal thin film, density of quantum dots in proximity to metal thin films, etc. This project is a preliminary investigation towards the same.

Hence, the focus of the project is on the following:

1. Understanding optical response of semiconductor quantum dots (excitons)
2. Understanding optical response of metal thin films (surface plasmons)
3. Creating semiconductor-metal nanostructures by Electron beam lithography
4. Observation of Luminescence from semiconductor-metal nanostructures

Figure 1.1: Schematic representation of interaction between excitations in semiconductor quantum dot to that in metal thin films
2.1 Quantum Dots and Excitons

As defined by Fahlman\textsuperscript{2}, nanocrystals are crystalline particles having at least one of the dimensions less than 100 nm. Quasi-spherical nanocrystals with dimensions less than 20 nm are known as quantum dots.

When a photon of sufficient energy is absorbed by a quantum dot, an electron gets excited to the conduction band leaving a hole in the valence band. If the surrounding medium does not have sufficient charge to screen the electrostatic Coulomb interaction between excited electron and the hole completely, then the excited electron and the hole can lower the energy by being as close as possible. Hence, such electron-hole pair behaves like a pseudo particle known as exciton.

If the size of the nanoparticle is smaller than separation between the electron and the hole, this electron-hole pair gets spatially confined, thus causing quantization of the energy levels. The position wave functions of the electron and the hole define the separation of the electron-hole pair, which is known as exciton Bohr radius. The typical range of values for exciton Bohr radius for semiconductor quantum dots is 1-10 nm.

The binding of the excited electron to the hole is similar to that in Hydrogen atom. However, electrostatic Coulomb force between the electron and the hole gets screened
due to the presence of other electrons inside the quantum dot. Consequently, the exciton Bohr radius is much larger than the radius of excited Hydrogen atom.

As mentioned by Brus\textsuperscript{3}, the Molecular Orbital theory provides a novel way to view energy levels of excitons inside a quantum dot as that of a molecule. Electron in the valence orbital of a molecule can absorb a photon to get excited to a higher molecular orbital. Similarly, in case of an exciton, the excited electron can be thought to occupy lowest unoccupied molecular orbital (LUMO), and the hole created can be thought to occupy highest occupied molecular orbital (HOMO). The LUMO and HOMO energies associated with the excited electron and hole can be found from the Schrödinger equation for the system. The energy difference between the LUMO and HOMO levels is hence the energy band gap.

Note that parallel or anti-parallel alignment of spins of the excited electron and hole can result in exciton fine structure due to exchange interactions. However, a detailed treatment of this phenomenon is beyond the scope of this thesis.

2.2 Luminescence from Quantum Dots

The excited electron can recombine with hole in the valence band by spontaneous emission of a photon. This phenomenon is known as Luminescence. The excited electron can have anti-parallel alignment of spin relative to the electron in the lower energy orbital. Corresponding excited state is known as singlet-excited state. Spontaneous
emission associated with decay of singlet excited state electron back to lower energy orbital is called Fluorescence. The excited electron can also have parallel alignment of spin relative to electron in lower energy orbital, which is known as triplet-excited state. However, by Pauli's exclusion principle, the electrons in same energy level differ in alignment of spins, and hence for emission from triplet excited state change of spin orientation is necessary. Thus, emission associated with decay of triplet excited state, which is known as Phosphorescence, has much lower emission rate than Fluorescence.

Quantum dots can absorb light with frequencies higher than their absorption edge and then undergo non-radiative relaxation to attain an energy level from which the emitted radiation would be at their peak luminescence frequency. This makes quantum dots interesting candidates for “frequency conversion” and several other promising applications in Nanophotonics.

Brus first discovered experimentally that the semiconductor quantum dots have energy band gaps that are dependent on its size, and hence, a shift in the fluorescence spectrum towards (blue) higher energy limit is observed. Hence, allowed frequencies for absorption and emission of photon are highly size-dependent in case of quantum dots.

The electron and the hole can recombine by a completely non-radiative recombination such as Auger-like process. The probability of such transitions however is dependent on the type of the quantum dot.
2.3 Semiconductor (Cadmium Selenide) Quantum Dots

Semiconductor quantum dots can be suspended in a chemical solvent that is chosen according to the type of quantum dots forming a colloidal solution. Such colloidal semiconductor quantum dots have provided tremendous understanding of physical and chemical properties at the nanoscale. However, to use a colloidal solution for practically usable devices can be quite challenging. Hence, for practical purposes, the quantum dots are embedded in a special type of solid-state matrix such as a polymer.

Figure 2.1: TEM of Cadmium Selenide quantum dot with a radius of 3.9 nm

Cadmium Selenide (CdSe) quantum dots are popular because of their high optical yield. Various theoretical models and experiments for synthesis of high quality CdSe quantum dots have been developed.
When in Wurtzite structure, Cadmium Selenide is a semiconductor with a direct band gap of nearly 1.74 eV (nearly 715 nm) in bulk form. In comparison with other semiconductors, Cadmium Selenide has a narrow energy band gap, and hence has a larger dielectric constant. Due to this, the electrostatic columbic attraction between the excited electron and the hole is significantly weaker because of the screening effect produced by other electrons within the quantum dot. Hence, such excitons have a loosely bound pair of excited electron and hole. As a result, they have a much larger spatial extent in comparison with the lattice constant of constituent material. Such excitons are known as Wannier excitons.

### 2.4 Introduction to Effective Mass Approximation Model

One of the many theoretical models to understand Wannier excitons in quantum dots is the Effective Mass Approximation (EMA) model proposed by Brus\textsuperscript{10} in 1986. One of the
ways to analyze this model is by considering exciton as a two-body problem consisting of the excited electron in conduction band and the hole in the valence band.

In long wavelength limit, the electron and hole wave functions can be assumed to be uncorrelated Bloch waves. Moreover, the masses of the excited electron and the hole can be considered to subsume the effect of the localizing potential by replacing them with corresponding effective masses. In addition, the Hamiltonian can have polarization terms to incorporate the effect of the potential that exists due to polarization charge induced at surface. Hence, the model Hamiltonian for the system is

\[
H = -\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{\hbar^2}{2m_h} \nabla_h^2 - \frac{e^2}{\epsilon |r_e - r_h|} + \text{(polarization terms)} \cdots \cdots \cdots \cdots (1)
\]

Where

- \( m_e \) is effective mass of the electron
- \( m_h \) is the effective mass of the hole
- \( \epsilon \) is the ambient static dielectric constant

Because the effective masses of the electron and the hole subsume the effect of the localizing potential, their values are significantly lower than the free electron mass. The dielectric constant in electron-hole interaction term incorporates screening of cumbic interaction. The analytical expression for total ground state energy is
E \simeq E_{\text{bulk}} + \frac{\pi^2\hbar^2}{2R^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{eR} - \text{(smaller terms)} \hspace{1cm} (2)

Where

- $E_{\text{bulk}}$ is the binding energy (negative) of bulk exciton
- $e$ is electronic charge in electrostatic units
- $R$ is the radius of the quantum dot
- $r = |r_e - r_h|$ is the exciton Bohr radius

In case of semiconductor quantum dots, the polarization terms are absent. Hence, the expression for energy would not have the “smaller terms” that are responsible for increase in the exciton energy.

Hence, the binding energy of a confined exciton in a semiconductor quantum dot differs from the bulk exciton, as it decreases due to quantum confinement term proportional to $R^{-2}$, and increases due to coulombic attraction term proportional to $R^{-1}$. In addition, for smaller values of $R$, the energy band gap is always larger, suggestive of the blue shift in absorption or emission spectrum.

Using separation of variables, Schrödinger equation for the model described above can be separated in two parts: one describing center-of-mass motion, and another describing relative motion. Schrödinger equation for the binding energy is analogous to the Hydrogen atom problem, and the energy levels of the exciton form an infinite series of
discrete energy levels below the one-electron conduction band, which changes with the wave vector because of the motion of exciton about its center of mass. In addition, the exciton Bohr radius of Wannier exciton can be expressed in terms of the radius of Hydrogen atom \(a_0\) as

\[
r = m_e \left( \frac{1}{m_e} + \frac{1}{m_h} \right) a_0
\]

The exciton Bohr radius for Cadmium Selenide is hence nearly 6 nm.

2.5 Introduction to Empirical Pseudo-potential Method

In spite of some level of success of Effective mass approximation model, there are several drawbacks in this model. Clearly, the excited electron and the hole can have either parallel or anti-parallel spins coupled by exchange interaction, but the corresponding interaction term is absent in the Effective mass approximation Hamiltonian. Further, Krishna et al have stated\(^{12}\) that the Effective mass approximation model considers a spherically symmetric potential inside the quantum dot with infinite potential barrier at surface. In addition, the effects of changes in lattice constant due to small size of quantum dot and at the surface are ignored. Moreover, the effective masses of excited electron and hole are assumed constant, which is not true except at band edges\(^{13}\). To overcome these drawbacks, they proposed Empirical pseudo-potential method.
The aim of this method is to solve the Schrödinger equation for electron in band n with wave vector \( k \). This many-body problem can be reduced to a form that can be solved numerically by making following approximations:

(1) Nucleus of the atom along with all electrons in inner shells is treated as the core (Valence-electron approximation)

(2) Every valence electron experiences mean field generated due to its core and other valence electrons.

(3) The core, being much heavier than valence electron, is considered to be fixed to corresponding lattice site (Born-Oppenheimer approximation)

With these approximations, the potential experienced by a valence electron is replaced by a pseudo-potential \( V_p \), which is a linear combination of spherically-symmetric pseudo-potential at all atomic sites. Such pseudo-potential is used in the Hamiltonian matrix, which, along with the Schrödinger equation for valence electron, is used to determine the energy band structure in a Wurtzite structure using numerical calculations.

### 2.6 Metal (Gold) Thin Films and Plasmons

In comparison to semiconductors, metals have approximately 10,000 times higher free electron density. In addition, there is a possibility of inter-band transitions\(^\text{14}\) by incident photons of sufficiently high energy (>1 eV). Hence, there is a vast difference in response of metals and semiconductors to external electromagnetic fields at optical frequencies.
The Free electron model provides elegant description of metal properties based on classical picture of free electrons moving in the mean field produced by static ion cores. In presence of external electromagnetic field, polarization causes accumulation of excess charge on the opposite surfaces. If the external electromagnetic field is oscillating, the free electrons collectively oscillate at the frequency of the applied field due to the restoring force offered by the static positive ion cores. Using such simple harmonic oscillator model for electrons oscillating with frequency $\omega$ and relaxation time $\tau$, the dielectric function can found to be

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega+i\tau)} \quad \cdots \quad (4)$$

Where

$$\omega_p = \sqrt{\frac{ne^2}{\varepsilon m}}$$

is known as plasma frequency

$m$ is the optical mass of the electron

$n$ is the number density of electrons

The resonant frequency (where the dielectric constant changes sign from negative to positive, and its real part goes to zero) is known as plasma frequency, and the collective oscillation of the free electron gas is called plasmon. The bulk plasma frequency for Gold is $1.38 \times 10^{15}$ Hz.
Hence, the optical response of bulk metals can be classified into three regimes: absorbing, reflecting, and transparent, depending on nature of dielectric function in various ranges of the product $\omega \tau$.

The optical response of metal nanoparticle is dependent on its size, free electron density and the difference of dielectric functions of the metal and surrounding medium. When a metal nanoparticle has at least one dimension comparable to the electron mean free path of its bulk form (the electron mean free path for Gold is around 50 nm), then the dielectric function differs from that of its bulk form, and hence the optical response of the nanoparticles changes from that of larger nanoparticles.

Similar excitation is possible when photons are incident on a metal thin film surrounded by a dielectric material\textsuperscript{16}, which is known as surface plasmon. Corresponding surface charge density oscillations are localized in one dimension, and are accompanied by an electromagnetic field that exponentially decays with distance from the metal thin film surface. Further, in special circumstances like suitable surface roughness, surface plasmon can interact strongly with incident visible light to create surface electromagnetic wave known as surface plasmon polariton, which can cause concentration of electromagnetic fields at the metal thin film surface.
Chapter 3: Introduction to Electron Beam Lithography

3.1 Introduction to Lithography
Lithography is a process to create patterns on a specific thin film on a substrate. For this purpose, a collimated beam of energetic particles of sufficient energy is incident on the thin film, which causes changes in its physical or chemical composition. This process follows selective removal of those parts of thin film that are either exposed or not exposed to the beam by use of chemicals or some etching process.

The beam particles can be electrons, photons, ions, etc., which have varying range of energy. If an electron beam is used to induce changes in the composition of the thin film, then the process is called Electron beam lithography. Ernst Abbe showed that the maximum resolution of an optical system is inversely proportional to the wavelength of its source\(^\text{17}\). Hence, Electron beam lithography produces patterns of very high resolution.

The thin film on which the pattern is to be created is known as resist. Generally, it is composed of a typical combination of a specific polymer (or its precursor) that is sensitive to the electron beam, and some chemical solvent, whose choice is based on the application of final product.

A dedicated Electron beam lithography setup is very expensive, and hence for research purposes, a Scanning Electron Microscope is appropriately modified to function alike.
Figure 3.1: JEOL 6400 SEM modified for Electron beam lithography

Figure 3.2: Optical column of the JEOL 6400 SEM
3.2 Choice of the Substrate

The substrate on which the thin film of the resist material is created can be either a metal or a semiconductor. The material chosen for substrate is generally a good conductor of heat and electricity, such as doped Silicon. If an insulator is used for this purpose, it can cause errors in nanoscale patterns\(^{18}\), as it would be unable to ground the charge and heat deposited by the electron beam.

The most important property that determines the choice of material for the substrate is its adhesion to the thin film that has to be created on it. If the adhesion is poor, then entire thin film might get removed while processing it with chemicals. There are several methods (based on the choice of resist and substrate) that induce physical or chemical changes in the substrate to have better adhesion of thin film.

3.3 Material for the Resist

The choice of the material for the resist depends on the application of final product. Primary function of a resist is to induce changes in its composition in response to the electron beam such a way that a precise latent image is formed. Usually a balance has to be sought between resolution and sensitivity to the electron beam, as the resist materials that provide high resolution are found to have low sensitivity to the electron beam.

There are two types of resists based on the way pattern is to be created: positive resist and negative resist. This is known as the Tone of the resist. Positive resists are those in which
the parts that are physically or chemically changed due to energy deposition by electron beam are removed during the development stage. Whereas negative resists are those, in which the parts that are physically or chemically changed due to energy deposition by electron beam remain after the development stage.

Positive resists usually made of a typical combination of a high molecular weight polymer dissolved in an appropriate chemical solvent. When the electron beam is incident on the sample, secondary electrons are created due to inelastic collisions with the resist material. These secondary electrons can break the chemical bonds of the polymer chains in such a manner that the affected parts of the resist material have significantly lower solubility than the unaffected parts of resist material.

3.4 Spin-coating Method

A thin film of the resist material is applied to the substrate by spin-coating method. The thickness and uniformity of the thin film can be controlled by changing various parameters involved in spin-coating process.

The procedure begins by cleaning the substrate. The substrate is cleaned by immersing it in specific cleaning agents for a specific time. Then these cleaning agents are removed from the substrate by washing it in de-ionized water. Then the substrate is observed under an optical microscope to check the density of impurities such as dust particles. If required, the substrate can be further cleaned using a Carbon Dioxide snow jet.
These clean samples are taken to spin-coating device for deposition of thin film. The substrate is held by vacuum on a table that can spin the substrate at a controlled speed. Few drops of resist material are put to cover the substrate completely, and then it is allowed to spin at known speeds for specific time. If the drops of resist material are not uniformly placed, sample is first spun at a low “spread-speed” for few seconds (especially when the solid content in the resist material is more, and hence viscosity is more), and then spun at higher “spin-speed”. Evidences suggest that the thickness of the resulting thin film depends more on the solid content (viscosity) of the resist material than the molecular weight of the polymer used. For example, at same spin-speed, 495K PMMA with 4% solid content is known to form a thicker layer than 950K PMMA with 2% solid content because of higher viscosity, even though its molecular weight is lesser\(^{19}\). Large angular acceleration is favored from one-step to another in the process.

For a specific resist material, data sheets are available from the manufacturing companies that describe the parameters required to attain a specific thickness. For example, the figure below shows what thickness of 950K PMMA resist material (with 2, 4, and 7 percent solid content in Anisole – A2, A4, A7 respectively) can be achieved by what spin-speed, if spun for a period of 45 seconds followed by dynamic spread for 5 seconds at 500 rpm. This data is from “NANO™ PMMA and Copolymer” data sheet by MICROCHEM Polymers.
3.5 Baking the Resist

Then the substrate with the thin film of resist material is baked on a hot plate or in an oven at a fixed temperature for specific amount of time. These parameters, which are usually provided by manufacturing companies, also depend on the type of resist material used. Most of the chemical solvent in the resist material is evaporated while baking. Hence, this process imparts appropriate viscosity to the thin film, which is necessary for Electron beam lithography. Moreover, adhesion of the thin film to the substrate is enhanced during this process. The sample is now ready to be patterned by Electron beam lithography.
3.6 Components of Electron Beam Lithography Device

Due to considerable progress in the field of electron optics, the Scanning Electron Microscopes modified to function as Electron beam lithography device are getting significantly better.

There are four major components of such a device: Electron Source to emit electrons, Optical column to control the electron beam, Sample chamber to place the sample for exposure, and a Computer with appropriate software to instruct the device to create desired pattern.

Like any Scanning Electron Micrograph, ultra high vacuum is required for a good quality electron beam. High vacuum minimizes the deflection of the electrons by the air molecules, and protects the sample from impurities floating in air. To achieve this, a set of two or more pumps is used to attain low-pressure levels within the Optical column. Still there can be some acoustic noise, which is minimized by padding the interior of the Optical column appropriately.

Moreover, the quality of the beam can be reduced due to mechanical vibrations created by vacuum pumps and other devices. This is avoided by having the Optical column relatively floating about the base.
Figure 3.4: Schematic diagram of a SEM modified for Electron beam lithography
In addition, external electromagnetic fields can influence the electron beam – the electron beam can fluctuate at a frequency of external electromagnetic fields. This is reduced by having the Optical column well shielded by a metal enclosure.

After the electron beam is emitted from the source, it passes through set of circular holes while moving from one component to another inside the Optical column, which are known as apertures. Apertures affect the shape and sharpness of the electron beam. Proper choice of aperture can reduce the effects of aberrations due to filament\textsuperscript{21}.

Electron source: This consists of a filament that creates electron beam by thermal emission of electrons in presence of external electromagnetic field, and a pair of electrodes to accelerate the electrons towards the anode to impart required intensity to the electron beam. The tip size of the source, the filament current, and dispersion of energy of the electron beam are important parameters to have a good electron beam profile.

Optical column: The first part of an Optical column usually consists of a Beam Blanker, which can deflect the beam away from the optical axis without turning the beam off. This is quite helpful, as frequent changes in filament current can damage the Electron Source. Usually it has a set of plates that can be charged electrostatically, and a Faraday cup mounted directly above the sample to measure the electron beam current through the Picoammeter. The potential drop required on the plates for blanking the beam is dependent on the beam energy. Hence, the Beam Blanker is connected to computer
control that can measure the beam current, and then induce proper electrostatic potential on the plates in order to achieve proper beam blanking.

The second part of an Optical column consists of a Lensing mechanism to adjust the diameter of the electron beam. Most common configuration consists of a set of three plates, amongst which the first and the last plate are electrostatically grounded, and the middle plate can have a very precise electrostatic charge, so that the beam can be collimated in a desired manner. This mechanism is known as electrostatic lensing. However, the electrostatic lenses can produce more aberrations, and hence magnetostatic lensing is preferred\textsuperscript{22}, which consists of coils that generate magnetic field such that the electron deflects towards the optical axis.

![Figure 3.5: (A) Electrostatic Lensing (B) Magnetostatic Lensing](image-url)
The third section of the Optical column is the Deflection unit, which deflects the electron beam on various regions of the sample surface. Just like the Lensing mechanism, Deflection unit could be electrostatic or magnetostatic. Correspondingly, a set of plates or coils is placed in such a way that an electrostatic field is created perpendicular to the optical axis or a magnetostatic field is created parallel to optical axis. The magnetostatic system produces lower aberrations, but the electrostatic system responds faster.

Sample chamber: The sample is mounted on a sample holder, and is placed on a stage inside the vacuum chamber. The Scanning Electron Microscope modified for Electron beam lithography is facilitated with an automated stage that can have horizontal movement with a precision less than a micron, and can have rotation and tilting of sample with a precision less than a minute. Precise control of the stage is necessary to create a periodic pattern on the resist.

The vertical distance of the sample from the electron beam emerging from the Optical column, which is known as the Working distance, has a significant impact on the quality of pattern generated. Working distance can affect the minimum spot size that can be achieved for the electron beam. Moreover, optimal magnification for a device also depends on the Working distance. Usually smaller Working distance is better, as the electron beam has lesser influence from deflections by air molecules, and external influences such as electromagnetic fields.
Computer Control: This component controls parameters such as beam spot size, exposure time for the smallest area that can be considered as a point on the sample (Pixel), amount of charge deposited on a pixel (Dose), beam blanking and deflecting the electron beam by setting appropriate voltages on corresponding coils etc. As shown in the figure, many components are connected to Computer control to have as much precision and automation as possible.

The Computer also has a CAD interface that is capable to create patterns that can be understood by software (NPGS) that instructs the hardware to perform necessary actions on other components to control the electron beam. The CAD has an easy to use graphical user interface. It provides all facilities for creating proper design files like insertion of basic geometrical figures and text. Then the file is saved as a two-dimensional design file in NPGS mode. This file is used to generate Run files that allow the user to set various beam parameters for writing the pattern.

The maximum area that can be scanned just by deflecting the electron beam (without moving the stage) is known as field size. The field size is limited by the magnification of the Scanning Electron Microscope used for Electron beam lithography. Every device has specific values of magnification for the best possible pattern quality. This is because of the highest possible signal to noise ratio for that magnification, which also depends on other components of that device. When the pattern is very large, its small features can be
“stitched” to each other in several writing fields so that the advantage of having high magnification is not compromised in order to create large pattern.

The sample is exposed to the electron beam mostly by Vector scan. This method involves scanning only those areas where the pattern is to be exposed, and hence it reduces the total time for the process. Moreover, if Vector scan method is used, then the pattern can also be created without a Beam Blanker. The Computer is connected to DAC converter that changes the digital signal to proper potential on the deflecting coils and plates. DAC converter of 16 bits by 16 bits would divide the field size into 65536 by 65536 smallest possible points for exposure, each known as a Pixel.

![Diagram](image)

Figure 3.6: Point-to-point spacing

The pattern is created by movement of the electron beam on the resist in discrete set of points, which induces physical or chemical changes that produces regions that serve as
latent image, which materializes during the development stage. As the electron beam moves on the surface, the distance between two consecutive points on the resist that are exposed is known as center-to-center spacing. A filled area is exposed point by point, and one line at a time. The perpendicular distance between two closest possible lines is known as line-to-line spacing.

3.7 Parameters of Electron Beam Lithography

Several parameters should be taken into consideration while setting the Electron beam lithography device for optimum performance.

Focusing of beam: The electron beam is converged and deflected multiple times in order to focus it on the resist. If the electron beam is not focused well, the area exposed is larger than intended. Hence, the electron beam does not travel in a single Pixel line. Moreover, the number of electrons incident per area also changes locally, which affects the required depth of the pattern.

In addition, like any optical system, the Optical column can have aberrations. For example if the electron source emits significantly wide spectrum of electron energies, then chromatic aberrations arise. To avoid chromatic aberrations, beam stability should be established by allowing the beam to be “on” for a couple of hours at a steady filament current before writing the pattern. Aberrations such as Astigmatism would arise if the
column is not aligned properly, or because of the improper converging of the electron beam by electromagnetic lenses and deflecting coils.

Focus of the electron beam must be adjusted near the edge of the Sample holder, until a clear image is visible on the display screen. One way to check the focus of the electron beam is to create a Contamination spot. For this, the electron beam is incident on the sample, at a high magnification (50,000 for JEOL 6400 SEM), close to the area where the image has to be created. Then the beam is allowed to burn the sample for a few seconds (make sure that the NPGS mode is on). This shall leave a small spot (tens of nanometers in diameter) where the electron beam hits the sample. If the spot is not circular, then the focus should be re-adjusted. It is advisable to do the same procedure multiple times in order to check the focus, as it is also possible that the layer of the sample is not uniform.

Electron dose: The Electron Dose is defined in terms of Dot dose, Line dose, or Area dose. Correspondingly, it is defined as a ratio of product of beam current and exposure time to unity, line length, or area respectively. Electron dose is a function of beam intensity, pixel size, exposure time, and characteristics of the resist (low molecular weight polymers require lower doses). The minimum Dose required for an appreciable change in composition of the resist by incident beam energy is known as Clearing Dose.

Dwelling Time: Dwelling time is the amount of time for which the electron beam is incident on a particular spot while writing the pattern. This, along with electron beam
intensity and resist sensitivity, are important factors for creating a good quality latent image on the resist. If Dwelling time is more than that required by resist, it can cause more electrons to be incident on the resist, and hence only a large spot is seen after the development of resist. If the dwelling time is set lower than that required by the resist, it can result in underexposed pattern, and hence not all the features shall be visible after developing the resist.

Sensitivity: Sensitivity is the measure of the effect of particular electron beam intensity on the resist. When the electron beam is incident on the resist, the energy deposited by the beam can cause physical and chemical changes to the resist material, and hence a latent image is created on the resist. The measure of physical or chemical change that the electron beam can cause to the resist is known as its Sensitivity. The Clearing Dose for a given material also depends on its Sensitivity.

Magnification: The allowed magnification range is divided set of small ranges, which is further divided into discrete values. Every small range has its own circuitry within the microscope, and hence there is an audible click on entering the next small range. The best signal to noise ratio (and hence the optimal magnification) is usually at higher values of magnification within a small range.

Contrast: Contrast of a resist material is a measure of the depth of the resist material that is affected by the incident electron beam. Suppose, D₁ is the maximum electron dose that
does not cause any change in composition of the resist layer, and $D_2 > D_1$ is the minimum electron dose required to change the composition of the entire depth of the resist layer, then the Contrast for that resist material is defined as the following:

$$C = \left[ \log \left( \frac{D_2}{D_1} \right) \right]^{-1}$$

(5)

Figure 3.7: Normalized remaining thickness vs. Dose for positive resists

As shown in the figure, the Contrast can be measured using the slope of the linear part (positive slope for positive resist, and negative slope for negative resist) of Normalized remaining thickness vs. Dose curves.

3.8 Quality of Pattern

The resolution and depth of the final pattern depends on the choice of parameters at every step of the process of creating pattern.
Electron optics of the Scanning Electron Microscope modified to function for Electron beam lithography plays a vital role in quality of beam, and hence affects the quality of pattern generated.

Molecular dynamics of the resist material during the spin-coating stage and the development stage also affects the quality of the pattern. Some resists may swell during the development stage. This can produce stresses when the resist contracts during baking stage, which can cause deformation of the pattern. Moreover, this can adversely affect the adhesion of the thin film to the substrate.

Among all the parameters that affect the pattern quality by causing variations in interaction of the incident electrons with the resist, the most significant is the Coulomb interaction between the resist material and electrons of the beam$^{23}$.

As the incident beam travels further into the sample, the electrons are deflected beyond regions of intended exposure due to the forward scattering by resist material.

Moreover, when the collisions are inelastic, secondary electrons are emitted in all the directions, which broaden the exposed area. Such effect can cause changes in intended pattern on nanometer scale, and is known as Proximity effect. Proximity effect is especially important when the pattern requires large variations from the incident beam energy in exposed regions of the resist. Proper choice of Dose can reduce the degradation
in quality of the pattern due to Proximity effect. Most of the incident electrons usually pass through the resist layer, and undergo inelastic collisions with substrate material, and are scattered back into the resist layer. Hence, proper choice of thickness of resist layer, and proper choice of substrate material can reduce degradation due to Proximity effect. For the same reason, using high accelerating voltage for the electron beam also reduces degeneration due to Proximity effect, as most the electrons are back-scattered so deep into the substrate that they cannot reach the resist layer.

Also, if the alignment of the Optical column is not proper, there can be errors of the order of tens of nanometers while writing the pattern.

### 3.9 Developing the Resist

Development of the resist involves a chemical treatment of the resist material, to remove either the exposed or the unexposed regions. As described above, the exposed regions and the unexposed regions have a significantly different solubility for typical chemical solvents. Hence, such chemical solvents can be used to dissolve away the more soluble regions of the resist, thus creating a pattern on the resist.

In this process, the sample is immersed in such solvents for a specific amount of time, so that the exposed regions or the unexposed regions (depending on the Tone of resist) are dissolved faster than the other. This also suggests that if the resist is immersed for longer than prescribed time, it dissolves even the unexposed parts for positive resist (and exposed parts in case of negative resist), thus creating a distorted pattern. The
The development process is also dependent on the temperature of the Developer. The most common type of solvent is a typical combination of Methyl Isobutyl Ketone (MIBK) and Isopropyl Alcohol (IPA). The ratio of MIBK to IPA determines the resolution and sensitivity of the resist during the development stage. Higher ratios of MIBK to IPA result in more contrast, whereas lower ratios result in higher resolution.

The resist can be re-baked on a hot plate or in an oven for specific time to remove the residual Developer and moisture.

### 3.10 Poly Methyl Methacrylate (PMMA)

Polymethyl methacrylate is a Polymer available in different molecular weights (between 35,000 to 22,000,000). As the resolution of the pattern also depends on the molecular weight of polymer used, PMMA of different molecular weights can be used for different applications. PMMA is still the highest resolution positive resist material available for Electron beam lithography.

To function like a resist, a chemical solvent such as Toluene or Methanol is one of the ingredients along with PMMA. The choice of the chemical solvent also depends on the molecular weight of the PMMA, as PMMA with different molecular weights have different solubility in a typical chemical solvent.
Evidences suggest that solubility of PMMA exposed to the electron beam depends more on molecular size of the solvent than the molecular weight of the polymer. However, as lower solubility is expected in case of higher molecular mass, parameters such as Sensitivity and Contrast of resist material are inversely proportional to the molecular weight.

If PMMA is exposed to a very high electron dose, then it becomes cross-linked. Thus, the exposed regions are insoluble in certain Developers like Acetone, thus causing the PMMA resist to behave like a negative resist.

For development of PMMA resist, MIBK in IPA in a ratio of 1:3 provides low sensitivity and a high contrast, whereas a ratio of 1:1 enhances sensitivity (only if low Dose is used) without a significant loss of contrast. In addition, unlike many other resists, the PMMA resist does not swell while being developed using MIBK-IPA.
Chapter 4: Observation of Metal-enhanced Fluorescence

4.1 Principle of the Experiment

A motive behind the experiment is to understand the interactions between semiconductor quantum dots and metal thin films. For this, we first understand the interaction of Fluorophores with metal thin films.

Presence of a fluorophore near a metal surface can cause changes in emission intensity of fluorophores\(^2\). The fluorescence does not change at all for large separations. The emission intensity increases by decreasing distance between metal and fluorophore. However, fluorophores that are very close (~1 to 4 nm) to the metal surface show reduction of emission intensity\(^2\) because of damping of the dipole oscillations. This effect is known as Metal-enhanced Fluorescence\(^3\).

Three main processes are considered to be responsible for Metal-enhanced Fluorescence:

1. Non-radiative energy transfer between the excited states of fluorophores, which then emit the energy by radiation\(^4\). This is also known as Resonance Energy Transfer. Enhancements for different positions and orientations of metal thin films have been theoretically found\(^5\).

2. As described before, the metal thin films surrounded by dielectric material produce enhanced electric fields over the surface on interaction with the visible light. The fluorophores in proximity to metal thin films surrounded by dielectric
material can hence show enhanced emission of light because of the electric fields. There are several experimental\textsuperscript{31} and theoretical evidences involving simulations\textsuperscript{32} that suggest the same.

(3) Enhanced emission rates of the fluorophores due to interactions with metals.

The Fluorescence yield and the Lifetime are given by\textsuperscript{33}

\begin{equation}
Q = \frac{\Gamma \Gamma_m}{\Gamma + \Gamma_m k_{nr} + k_q}
\end{equation}

\begin{equation}
\tau = \frac{1}{\Gamma + \Gamma_m k_{nr} + k_q}
\end{equation}

Where

\( \Gamma \) is the radiative decay rate of Fluorophore

\( \Gamma_m \) is the radiative decay rate of Fluorophore near the metal

\( K_{nr} \) is the non-radiative decay rate of Fluorophore

\( K_q \) is the collisional quenching rate (determined by Stern-Volmer equation)

Note that as \( \Gamma_m \) increases, Lifetime decreases, and hence, emission rate increases.

Further, there are evidences that suggest that there could be energy transfer from excited states of Fluorophores to the surface plasmons, which then emit at a frequency characteristic of the Fluorophores\textsuperscript{34}. 
Moreover, various modes of surface plasmons are excited with change in the shape and size of the metal thin film. Hence, if fluorophores are randomly spaced from the metal thin film, there is a greater probability for them to get coupled to one or more surface plasmon modes, which can result in enhancement.

Similar effects are expected if quantum dots are used as Fluorophores. For this, the idea is to have a known density of quantum dots spread over a thin film of a known thickness. Following diagram describes outline of the process.

Figure 4.1: Various steps involved in the Experiment
4.2 Gold for the Metal Thin Films

Gold was chosen for the small metal thin films. Gold has higher intrinsic losses than several other materials (such as Silver) that have surface plasmon resonance peak in optical regime. This reduces the surface plasmon oscillations and broadens the surface plasmon resonance peaks. The advantage of using Gold however is its high inertness.

4.3 PMMA for the Resist

To create thin islands of gold, Electron beam lithography is used. The resist material chosen for this process was 950K PMMA with 4% solid content in Anisole. The advantage of using resist material with less solid content is that a more uniform thickness of resist layer can be achieved. Moreover, a high molecular weight PMMA provides high resolution and reasonably good sensitivity to electron beam, as mentioned in the chapter on Electron beam lithography.

4.4 Doped Silicon as the Substrate

Doped Silicon was chosen as the substrate material. The area of the substrate was around $2 \text{ cm}^2$. This substrate is known to have good adhesion to the PMMA resist material that was used. In addition, it is a good conductor of heat and electricity, which helps to remove the charge and heat deposited during Electron beam lithography.
4.5 Cleaning the Substrate

The substrate was cleaned by immersion in Acetone followed by immersion in Methanol for 2-3 minutes each. These cleaning agents were removed from substrate surface by washing it with de-ionized water. Then the water droplets were removed by high-pressure air spray. (The substrate should be observed under an optical microscope. The dust and other foreign material look like small shining particles with high luster, whereas the water droplets shining in various colors. If the density of foreign material appears to be more in certain regions, further cleaning with high-pressure Carbon dioxide snow jet is recommended).

4.6 Spin-coating the Resist on the Substrate

Then the clean substrate was taken to spin-coating device in order to cover it uniformly with a single later of resist material. The substrate was then held by vacuum on the surface of rotating table. Then the substrate was cleaned once again by Acetone and lens paper.

Then a few drops of resist material were put to cover the entire surface of the substrate. This method is known as Static dispense. Then the sample was spun for 5 seconds at spread-speed of 500 rpm so that the resist material spreads on the sample surface uniformly, and then it was spun at spin-speed of 3000 rpm for 45 seconds to achieve uniform thickness at nanometer scale. According to the data sheets provided by suppliers, the thickness of the resist material should be around 250 nm. The quality of the spread is
apparent from the uniformity of the color of the polymer layer formed. Even if there are changes in the thickness on nanometer scale, color changes due to interference effects of the thin film.

4.7 Baking the Resist
The sample was baked for nearly 80 seconds on a hot plate at 180 degree Celsius so that its adhesion with resist layer is enhanced and an appropriate amount of viscosity is imparted to the resist layer.

4.8 Creating Pattern by Electron Beam Lithography
Then the sample was taken for Electron beam lithography. A small scratch was made on one side of the sample so that the orientation of the sample inside the chamber can be known. Moreover, after mounting the sample on the sample holder, as a good practice, a sketch of the sample with the mounting screws was made. The sample was put inside the vacuum chamber. The accelerating voltage was set to 20 kilo-volts, and the filament
current was set to 65 micro-amperes. The Working distance was set to 15 mm. Then, after setting the probe current, contrast and brightness of the Optical column, the focus of the beam was adjusted at the edge of the Sample holder. When the electron beam is incident on the sample for patterning, the scanning mode of the microscope is set to off, and hence the XY coordinates of the sample were noted on the sketch of the sample, so that the area where the patterns have to be written is known. Once the Electron beam lithography is set to function, none of its parameters should be changed except electron dose (probe current) and magnification.

An array of isosceles triangles of nearly 5 µm height, and an array of 1 µm dots was patterned on separate regions of the sample. Very high area dose was used so that entire height of the resist layer undergoes a change in composition. After the latent image was created, the sample was carefully taken out of the device chamber in the reverse order it was put into the chamber.

4.9 Developing the Pattern

Then the sample was taken for development. MIBK with IPA in ratio of 1:3 was used as a Developer. The advantage of using this Developer is that it gives a high resolution to the patterns. Now the patterned area of the sample should be a layer of resist material with prism-shaped and cylindrical holes that extend all the way to the top of the substrate.
4.10 Sputtering Gold on the Sample

Sample was put in between two electrodes inside a chamber with Argon gas at low pressure. The top electrode functioned as cathode and bottom electrode functioned as anode. A planar gold target was placed just above the sample. Sufficient electric field was applied to the electrodes to ionize the Argon gas to form Plasma, which was magnetically confined up to periphery of the gold Target. As the ions from the ionized Argon gas collided with a planar gold target, gold atoms were ejected in random directions. These atoms got deposited on the patterned resist layer.

Figure 4.3: Sputter-coater

For sputter-coating, the rate of deposition of gold atoms was directly proportional to the Plasma current, the potential applied to electrodes, and time of deposition. Hence, by controlling the pressure of the Argon gas between the electrodes, the rate of deposition of gold atoms was set to be 0.3 nm/s (proportionality constant for the gold as suggested by
the sputter-coater suppliers is 0.17). Hence, a nearly 45 nm thick layer of gold should have deposited on the resist layer and within the holes created.

Figure 4.4: (A) Sputtering of gold atoms on the sample (B) Sputtered sample

4.11 Lift-off of the Coated Film

Lift off is a process in which the material that is coated on the sample (gold) is removed along with the resist material. Success of the lift-off depends on adhesion of the gold coating on the substrate, and on adhesion of the layer inside the holes to the top of resist surface through the sidewalls of the holes created. Moreover, as the gold atoms are ejected at random angles from the target during sputtering, lift-off has to be done carefully, as there is more probability that the sidewalls of the pattern are also coated. For good lift off, the coating thickness must be less than two-thirds of the resist thickness.

For this process, the sample was immersed in Acetone for nearly 20 minutes to dissolve the resist layer. The gold thin films that were deposited onto the substrate through the
holes in the resist layer should have remained. Hence, small islands of gold with a height of nearly 45 nm should have formed on the sample.

4.12 Spreading CdSe Quantum Dots on the Gold Thin Films

Cadmium Selenide quantum dots were chosen for this purpose because of their high optical yield. Core Cadmium Selenide quantum dots with emission peak at around 550 nm were purchased from Evident Technologies.

The quantum dots were in the form of a colloidal solution in Toluene at a concentration of 60 nmol/ml. The concentration was further diluted by mixing of 5 parts of Toluene with 1 part of obtained colloidal solution. This corresponds to $10^{-5}$ mol/l, or nearly 6000 nanoparticles per micron$^3$.

Few drops of this colloidal solution were put on the substrate, and then it was allowed to dry on its own. As the boiling point of Toluene is around 111 degree Celsius, it quickly evaporates leaving a layer of CdSe quantum dots along with some residue on the gold islands. Now the sample has an array of gold thin films with Cadmium Selenide quantum dots randomly distributed on it.
4.13 Illuminating the Sample with LASER

A simple and elegant modification of an optical microscope shown in the figure below was used to excite the system of quantum dots and gold thin films using a LASER, and observe the corresponding luminescence.

![Schematic diagram and photograph of modified optical microscope](image)

Figure 4.5: (A) Schematic diagram and (B) photograph of modified optical microscope connected to spectrometer

The sample was illuminated by 405 nm InGaN LASER using 500 nm filter, and observed under an optical microscope at 40 times magnification. The following figures show the images observed under the setup described above for the patterns of triangles and dots. Observation of enhancement of luminescence intensity from the semiconductor-metal nanostructures is suggests the coupling between excitations in semiconductor and metal.
Moreover, in case of the larger triangular patterns, it appears that the quantum dots have coagulated around the metal thin film. This is possible because of the surface tension created by evaporation of the Toluene. In addition, as there is no luminescence from the center of the metal thin films, possibly the luminescence in this case is coming from the quantum dots.

![Figure 4.6: Luminescence from the patterns of (A) triangles and (B) dots](image)

4.14 Scanning Electron Microscopy of the Patterns

The sample was observed in a Scanning Electron Microscope to see if the gold islands have been patterned properly. Upon observing at high magnification, it was found that the gold islands formed were distorted. The triangles that were patterned were distorted at the vertices, and the dots appeared to have elongated along the sweep direction of the beam. This could have happened because of improper focusing of the electron beam, or change
in composition of the resist layer beyond intended regions due to the high dose of incident electrons and corresponding secondary electrons.

Figure 4.7: SEM images of the pattern of (A) triangles, and (B) dots at increasing magnification
However, recently we have been successful in creating patterns of equilateral triangles of sides 5 \( \mu \text{m} \), and circles of diameter 1 \( \mu \text{m} \) on 950K PMMA A-4 resist by following the same procedure that is mentioned in the chapter above.

![Pattern of triangular gold islands (of 5 \( \mu \text{m} \) sides) (A) after Development, and (B) after Lift-off](image)

Figure 4.8: Pattern of triangular gold islands (of 5 \( \mu \text{m} \) sides) (A) after Development, and (B) after Lift-off

![Developed pattern of 1 \( \mu \text{m} \) dots on 950K PMMA-A4 resist](image)

Figure 4.9: Developed pattern of 1 \( \mu \text{m} \) dots on 950K PMMA-A4 resist
4.15 Luminescence Spectra of the Patterns

The next two figures are luminescence spectra from the CdSe quantum dots over the gold islands (pattern of dots), and from the CdSe quantum dots over the substrate (with apparently same density as on gold islands) respectively. These spectra were obtained for an integration time of 1000 milliseconds.

By comparison, it appears that the luminescence intensity from the CdSe quantum dots on gold islands was more ten times of that from CdSe quantum dots on the substrate, possibly due to interactions with gold thin film.
Figure 4.10: Luminescence spectra of the quantum dots over the gold thin film
Figure 4.11: Luminescence spectra from the quantum dots on the substrate
4.16 Conclusion

We fabricated an array of gold islands of nearly 45nm height on a doped silicon substrate. These thin films were observed by an optical microscope for the effect of a deposited layer of CdSe quantum dots under excitation with a 405 nm LASER (and 500 nm filter). The emission from quantum dots around the elliptical gold islands appeared to be enhanced by a factor more than 10. Extensive understanding of the working principles of Electron beam lithography, and a considerable background research on quantum dots was a part of the process.

4.17 Directions for Future Work

(1) Metal-enhanced Fluorescence is expected depend on the distance of quantum dots from the metal thin film. One of the ways to introduce such variations could be to coat the gold islands on the sample with a thin layer of the resist material again, and then distribute the colloidal quantum dots on top of it.

(2) Density of quantum dots over the gold thin film should be varied in order to check the luminescence enhancement factor, keeping other parameters fixed. Methods to have a precise control over the density of the quantum dots on the gold thin film surface should be found.

(3) The effect of shape and dimensions of the gold thin films on luminescence enhancement should be studied in more detail. Also, the distance of the gold thin films from each other, and different arrangements of the gold thin films with respect to each other should be studied in more detail.
(4) For a particular combination of angle of incidence of the LASER and dimensions of the gold thin film, the surface plasmon absorption in the gold thin film can differ. This way, difference in the intensity of fluorescence emission from quantum dots can be observed for different surface plasmon absorption by gold thin film in its proximity.
References


