Design and fabrication of self-assembled thin films

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ABSTRACT

Students experience the entire process of designing, fabricating and testing thin films during their capstone course. The films are fabricated by the ionic-self assembled monolayer (ISAM) technique, which is suited to a short class and is relatively rapid, inexpensive and environmentally friendly. The materials used are polymers, nanoparticles, and small organic molecules that, in various combinations, can create films with nanometer thickness and with specific properties. These films have various potential applications such as pH optical sensors or antibacterial coatings. This type of project offers students an opportunity to go beyond the standard lecture and labs and to experience firsthand the design and fabrication processes. They learn new techniques and procedures, as well as familiarize themselves with new instruments and optical equipment. For example, students learn how to characterize the films by using UV-Vis-NIR spectrophotometry and in the process learn how the instruments operate. This work compliments a previous exercise that we introduced where students use MATHCAD to numerically model the transmission and reflection of light from thin films.

Keywords: thin films, ionic self-assembled monolayers, spectrophotometry

1. INTRODUCTION

With the introduction of a quality enhancement plan[1] (QEP) a capstone course was developed in the Department of Physics and Astronomy at Virginia Military Institute (VMI). This capstone course is required in the Core Curriculum and it is offered as either a common class, or independent study, or Institute Honors. A recent increase in enrollment has influenced changing the course from a one-on-one independent study to a group lecture and laboratory setting, to accommodate a larger number of majors. Course offering is specific to a faculty's expertise and it creates a unique opportunity for students to apply knowledge learned in previous courses as well as have access to instrumentation and equipment that is otherwise not commonly found in a general physics laboratory. In addition, students learn and develop laboratory skills and knowledge in advanced fields. In this paper we present a project run in the capstone course in which students review and apply concepts in optics related to interference, thin films fabrication and characterization as well as thin film modeling using Mathcad programing.

The capstone course consists of two parts. The first part includes a detailed review of physics concepts, preparation for various tests (Physics GRE, ASTB, OAT), creating resumes, job and graduate school searches, and outside speakers or visits to nearby research laboratories or graduate schools. The second part of the course is dedicated to a laboratory experiment, in this case performed in the Thin Films Lab at VMI. Typical projects include thin films for various applications such as optical filters, photovoltaics, pH optical sensors, antibacterial coatings, and antireflection coatings.

At the beginning of the laboratory stage, students are given a lecture presentation on the ionic-self assembled monolayer (ISAM) film fabrication technique, the instruments and equipment used, and on safety in the lab (lab coats, goggles, gloves). During the introductory part, students also learn how spectrophotometers work, particularly the Perkin Elmer Lambda 900. They also work as a team on proposal writing for a VMI Wetmore grant that will supply part of the funds for lab expenditures. This is a beneficial learning experience for students as they will apply grant writing skills in their future careers. The advantage of using ISAM technique for this project is that, although it involves a team effort, each student is able to choose an individual project and take ownership of it. At the end of semester, they hand in a written final report and each give a presentation on their project.

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2. THEORY

In a previous paper[2] we developed an exercise for numerical modeling of thin film optical filters that introduced students to the topic of numerical modeling of optical properties for thin films. The exercise uses the transfer matrix constructed for each component layer in a coating. As an application of that exercise students are able to apply it to one layer ceria film using the following parameters: CeO_2 film thickness is 25 nm, index of refraction for CeO_2 is 2.35[3], index of refraction of quartz substrate is 1.55[4], and index of refraction of air is 1.00. Computing the transmittance over the visible range, it is found that at 200 nm, for example, the reflectance is 67%. The results of Mathcad program calculations for CeO_2 layer on a quartz substrate are shown in the transmittance spectrum in Figure 1.

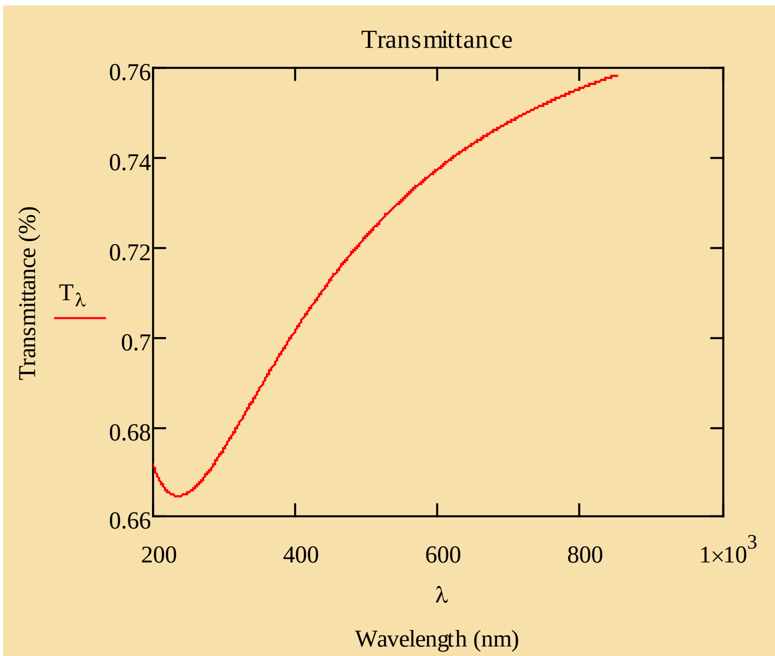

Figure 1. Calculated transmittance for a 25 nm layer of CeO_2 on quartz substrate.

3. EXPERIMENT

3.1 Ionic self-assembled monolayers (ISAM) technique

One of the film fabrication techniques used in this class is the ionic self-assembled monolayers (ISAM) also known as layer by layer (LBL) technique. This technique has been proven to yield uniform homogenous thin films with conformal qualities[5-6]. The technique affords control of thickness and composition at the nanometer level and, based on the materials selected, can be used to incorporate polymers, small molecules, nanoparticles, proteins, etc. in the films. In addition, the technique is environmentally friendly and is applied at room temperature and pressure. Overall, the ISAM fabrication technique is ideal for a variety of research projects as well as in class demonstrations. This deposition method consists of alternate dipping of a substrate in into an aqueous solution of a cation followed by immersion into an aqueous solution of an anion.

The ISAM technique enables deposition of the films on a variety of substrates, including glass and quartz that are used in this laboratory experiment. For these projects students also learn how to clean substrates and prepare them for deposition. In this particular case they clean the substrates by sonicating them in a solution of Micro 90 followed by sonication in deionized water and then drying with prepurified nitrogen. For films fabrication we use a combination of small molecules, nanoparticles, and polymers based on a specific application that students choose, such as optical pH sensors, photovoltaics, UV absorbent or antibacterial films[7]. Among the several projects chosen by students we discuss in detail the one based on cerium oxide (CeO_2) or ceria. Figure 2 shows an ideal representation of built ISAM films that contain nanoparticles (cerium oxide) and its counterion polymer.

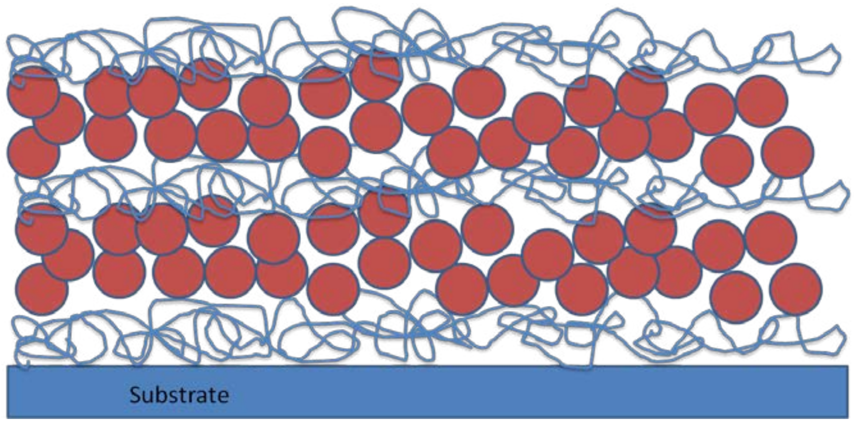

Figure 2. Schematic representation of ISAM films containing nanoparticles and polymers.

3.2 UV absorbent films

For this project students use 25 nm ceria nanoparticles to explore the feasibility of incorporating them into the ISAM films. These materials are suitable for various applications and are currently studied for antibacterial and antireflective properties. Nanoceria is also of interest as an anti-angiogenic therapeutic agent[8] and for its antiapoptotic effects[9].

Cerium oxide (< 25 nm diameter particles in solution) is purchased from Sigma Aldrich and poly(styrenesulfonic acid sodium salt) (PSS) from Polysciences, Inc. and are used as water based solutions, with pH=3.98 for cerium oxide solution and pH=6.00 for PSS. The index of refraction of CeO_2 is 2.35[3] and for PSS is 1.456.

The solutions are used without any pH adjustments. Further studies are in the works on the optimization of the solutions and how their parameters affect the thickness per bilayer and film response. The films are deposited on a quartz substrate because ceria absorbs in UV. The quartz substrate is immersed for ten minutes in each of the solutions followed by rinsing with deionized water in between the two solutions to remove excess material.

The absorption and transmission spectra are taken with a Perkin Elmer Lambda 900 UV-Vis-NIR spectrophotometer. Students take transmittance spectrum of ceria solution, shown in Figure 3, and of CeO_2/PSS film, shown in Figure 4. They observe that the optical properties of the ceria are transferred to the film.

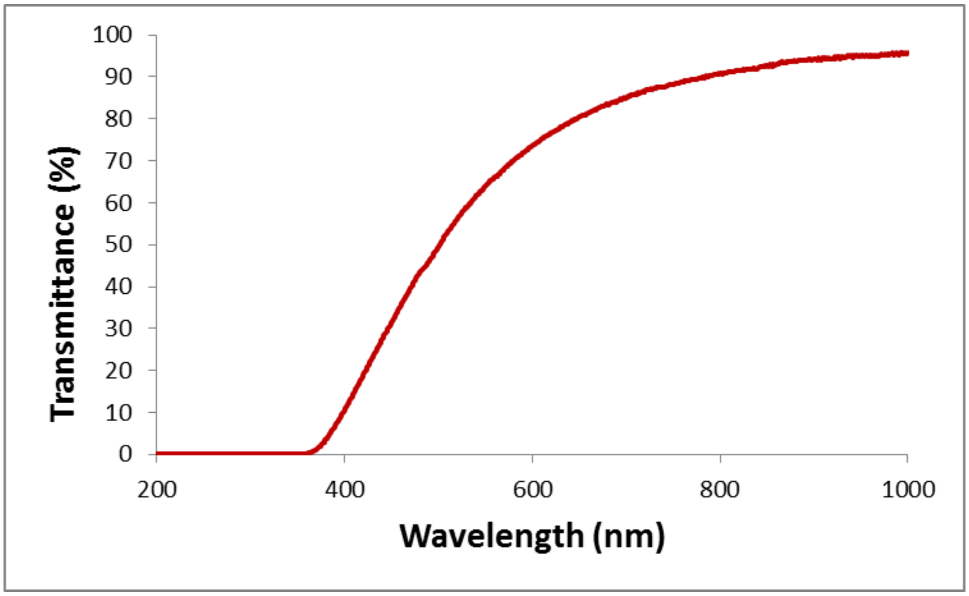

Figure 3. Measured transmittance of cerium oxide aqueous solution.

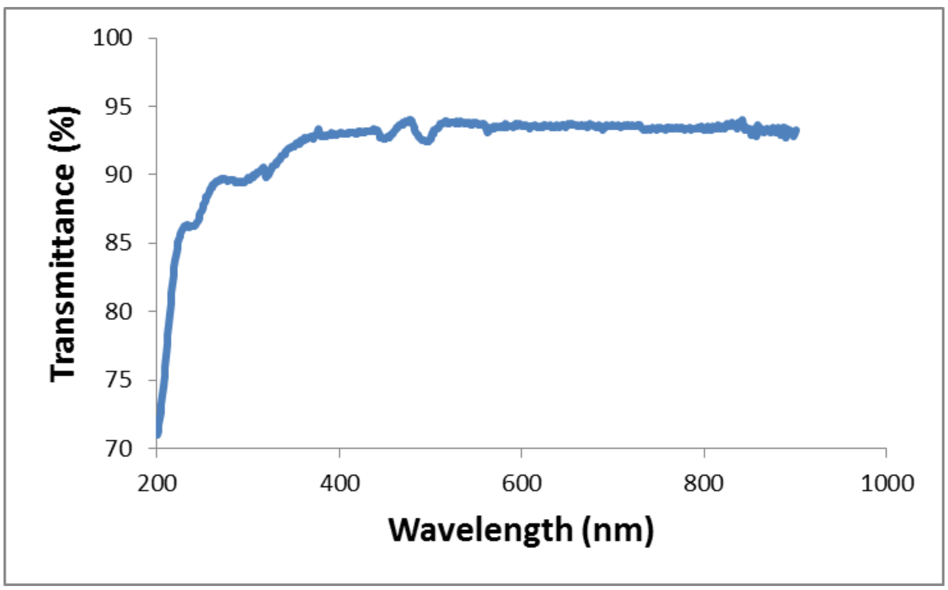

Figure 4. Measured transmittance of a layer of CeO_2 film on quartz fabricated with 25 nm nanoparticles.

The measured transmittance of one layer (25 nm) of ceria on quartz is shown in Figure 4, with a value of 71% at 200 nm, compared to the 67% calculated value. The almost 6% difference in values is mostly due to the fact that the ceria nanoparticles do not completely cover the substrate.

In addition to the comparison of theoretical and experimental values of the optical properties of the films students further explore other properties of CeO_2/PSS films by analyzing their absorbance versus the number of deposited bilayers (and therefore thickness). The results of this measurement are shown in Figure 5, which indicates that by using the ISAM technique with the combination of ceria nanoparticles and PSS, the films do build up in a uniform manner as more bilayers are added.

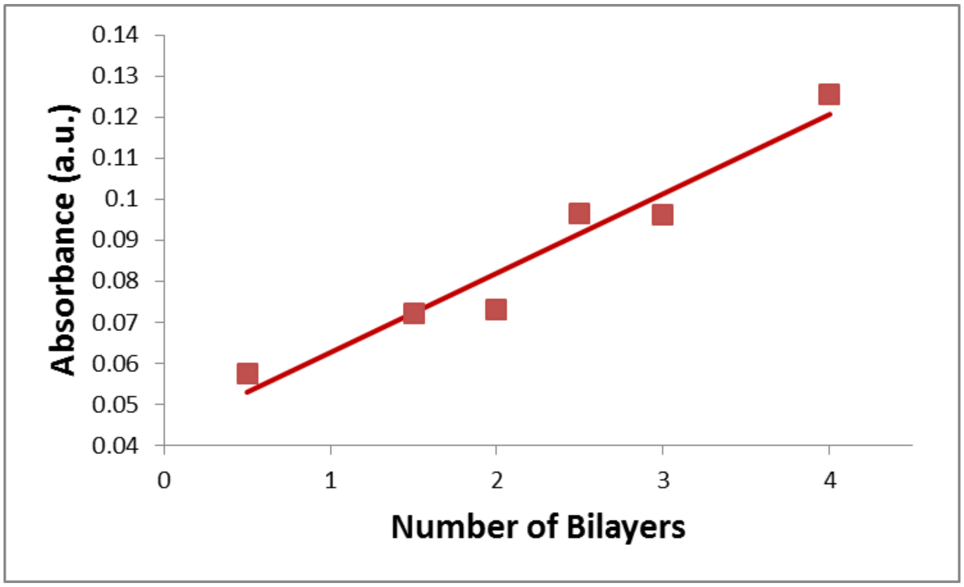

Figure 5. Absorbance vs. number of deposited bilayers for CeO_2/PSS films.

4. SUMMARY

We have described an effective method of engaging senior college students in a meaningful learning and research experience during the capstone course. The design and fabrication of thin films through ISAM method allows exploration of optical properties of thin films for various applications, ranging from optical pH sensors to antibacterial coatings. The students enjoyed the class and the hands on laboratory exercise. They found this experience very useful and meaningful.

The exercise includes the use of a Mathcad program to calculate transmittance for cerium oxide layer on quartz substrate and comparison with the transmittance measurements of a similar film fabricated by ISAM technique. The percent difference between the theoretical and experimental transmittance is less than 6% which indicates a relative good agreement.

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