Preparation of Xerogel Films Doped with R6G Laser Dye using spin coating technique and Study the Spinning parameters

Baha T. Chiad, Abbas J. H. Al-Wattar and Firas J. AL-Maliki

Department of Physics, College of Science, University of Baghdad, Jadiriya, Baghdad, Iraq

Abstract

Spin coating technique has been applied in this work to prepared Xerogel films doped with Rhodamine 6G laser dyes. The solid host of laser dye modifies its spectroscopic properties with respect to liquid host. During the spin coating process the dye molecules suffer from changing their environment. The effects of three parameters were studied here: the spinning speed, multilayer coating and formaldehyde addition.

Keywords
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تحضيرالاغشية الرقيقة من مادة الـ Xerogel المطعمة بصبغة الرودامين 6G الليزرية بأستخدام تقانة الطلاء البرمي و دراسة معلمات البرم

بهاء طعمة جياد ، عباس جاسم حمادي وفراس جواد المالكي

قسم الفيزياء- كلية العلوم - جامعة بغداد – الجادرية، بغداد، العراق

الخلاصة:

استخدمت تقانة الطلاء البرمي في هذا العمل من اجل لتحضير اغشية رقيقة من مادة ال Xerogel مطعمة بصبغة الرودامين 6G الليزرية. ان الوسط الصلب المطعم بالصبغات الليزرية يحسن المواصفات الطيفية للصبغات بالمقارنة مع الوسط السائل. اثناء عملية الطلاء البرمي تعاني جزيئات الصبغة من تغيرات في بيئة الوسط ةمن سائلة الى صلبة. تمت دراسةتاثير ثلاث معلمات في عملية التحضير : سرعة البرم، تعدد طبقات الطلاء و اضافة مادة الفورملدهايد.

Introduction

There are two main types of coating techniques, depending on the effect to be obtained and the material to be used, the gas phase vacuum and the wet coating techniques. The first one requires more equipments, high temperature and high cost. As general prerequisites for obtaining wet chemical coatings with high optical qualities on glass, it can be stated that the coating steps have to be carried out under clean room conditions.

There are many types of wet coating techniques such as spin coating, dip coating, spry coating, chemical coating, etc. Spin coating and dip coating are the most favored in the Sol-Gel technique [1, 2, 3, and 4].

Spin coating has been used for several decades for the application of thin films. A typical process involves depositing a small puddle of a fluid resin onto the center of a substrate and then spinning the substrate at high speed (typically around 3000 rpm).

Centripetal acceleration will cause most of the resin to spread to, and eventually off, the edge of the substrate, leaving a thin film of resin on the surface. The spin coating process can be divided into four major stages, as shown in Figure (1):

a. Deposition, which is the first stage of the spin coating process for delivering an excess of the liquid polymer to the surface of the substrate.

b. Spin – up, which is the second stage of spin coating, for covering or wetting the entire surface of the substrate with excess coating liquid?

c. Spin-off, which is the third stage of spin coating, for removing the excess liquid from the entire surface of the substrate.

d. Evaporation of solvents, which is the last stage of the spin casting process, where the liquid solidifies due to the solvent evaporation.

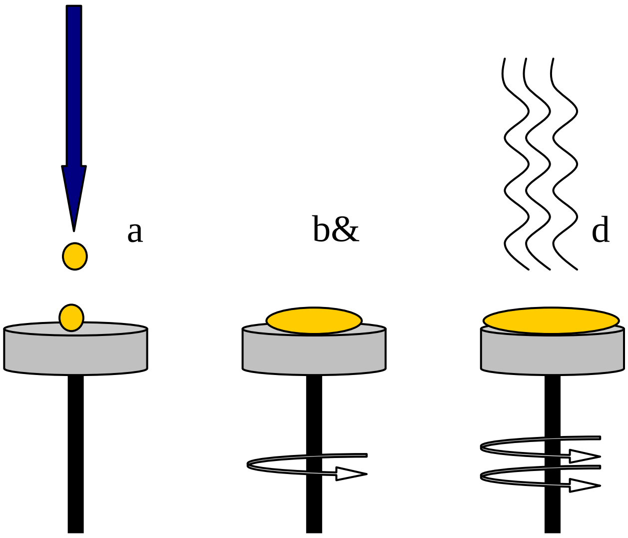


Fig. (1): shows the spin coating steps [5]*.*

Two common methods of dispense are Static dispense, and Dynamic dispense. Static dispense is simply depositing a small puddle of fluid on or near the center of the substrate. Higher viscosity and /or larger substrates typically require a larger puddle to ensure full coverage of the substrate during the high speed spin steps. Dynamic dispense is the process of dispensing while the substrate is turning at low speed [5].

In general, higher spin speeds and longer spin times create thinner films. Spin speed is one of the most important factors in spin coating. As the resin dries, the viscosity increases until the radial force of the spin process can no longer appreciably move the resin over the surface. At this point, the film thickness will not decrease significantly with increased spin time. The acceleration of the substrate towards the final spin speed can also affect the coated film properties, since the resin begins to dry during [6].

Chemical Material:

The following materials were used: tetraethylorthosilicate (TEOS) (Purity> 98%) was supplied by Schuchardt, Hohenbrunn, Germany; Ethanol was of Analytical grade, (Purity 99.9%), supplied by Gainland Chemical Company, U.K.; Rhodamine 6G, molecular weight 479.02 gm/M, Lc (5900), supplied by Lambda physik [7], Formaldeyde and hydrochloric acid HCl (0.15 M 37٪) supplied by Aldrich company, and Deionized water**.** Figure (2) shows the chemical structure of R6G dye.

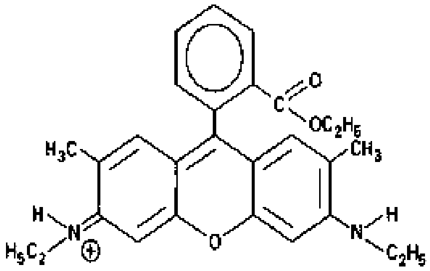


Fig. (2): The chemical structure of the R6G dye [7]*.*

The Xerogel film samples were prepared using Sol- Gel Technique. The two recipes mentioned in the flowchart, as shown in Figure (3), were tested. Where the laser dyes dissolved in ethanol at concentration of 5×10^{-4}M. Both recipes, normal recipe (route no.1) and formaldehyde recipe (route no. 2), were applied in this work. The details of the preparation process using Sol-Gel technique are mentioned elsewhere by Al-Wattar et al [8-9].

Measuring instruments:

Centra-5 UV-VIS spectrometer, supplied by GBC Scientific Equipment Pty

Ltd. (Australia), was used in this work for absorption measurements. Laser induced fluorescence of the dye has been produced using a diode pumped solid state green laser as a light source, of wavelength 531.5nm. The dye fluorescence emission was detected thought a Jarrell ash monochromatic model 82-000. This unit is an Ebert scanning spectrometer, 0.5 meter focal length, with eight speed electric drives, plane reflection grating of 1180 groove / mm.

The detection unit is a photomultiplier (type S666 Hamamatsu) which was connected to an X-Y/t recorder (SIEMENS) to record the out put signal.

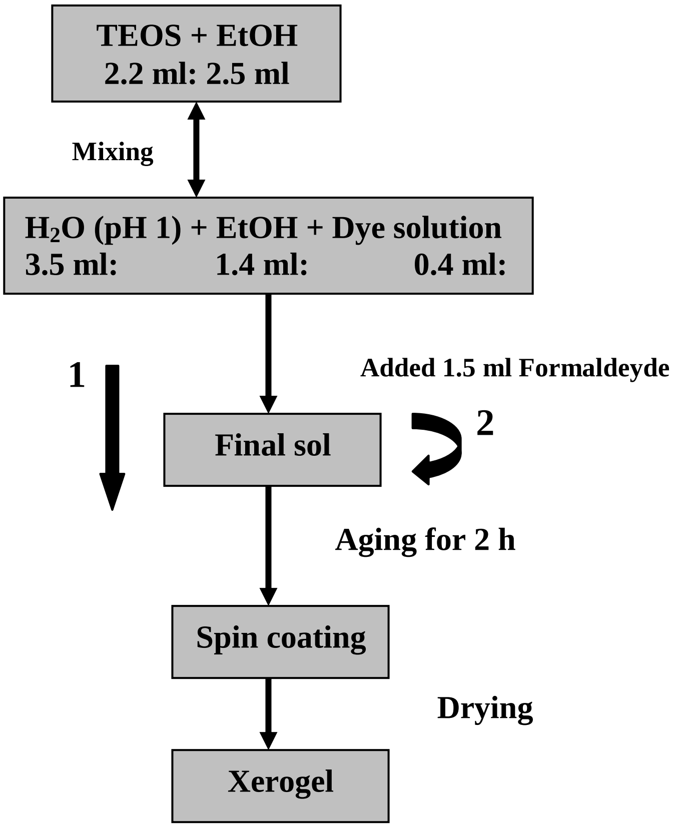


Fig. (3): Preparation procedure flowchart for normal and Formaldeyde recipes

Xerogel film testing:

Firstly the speed effects on the optical properties of the products were studied, since the speed is the most important parameter in the spin coating technique.

Four spinning speeds were chosen in this respect (2000, 2500, 3000 and 3500 rpm), according to the practical requirements, to produce films with the desirable properties.

Figures (4-a, b) shows the speed effect on the absorption spectra of R6G film samples at 10^{-4} M of one and two layers respectively. This dye has neat and structured spectra for all the spinning speeds. Figure (4-a), for one layer samples, shows that the peak of absorbance increased as the spinning speed increased reaching a maximum value at about (3000 rpm) and then decreases(see also Figure(5). While in the case of two layers the peak absorbance decreases monotonically as spinning speed increases.

This study focuses upon R6G dye, because of its high photochemical and photophysical stability and large absorption cross section [10].

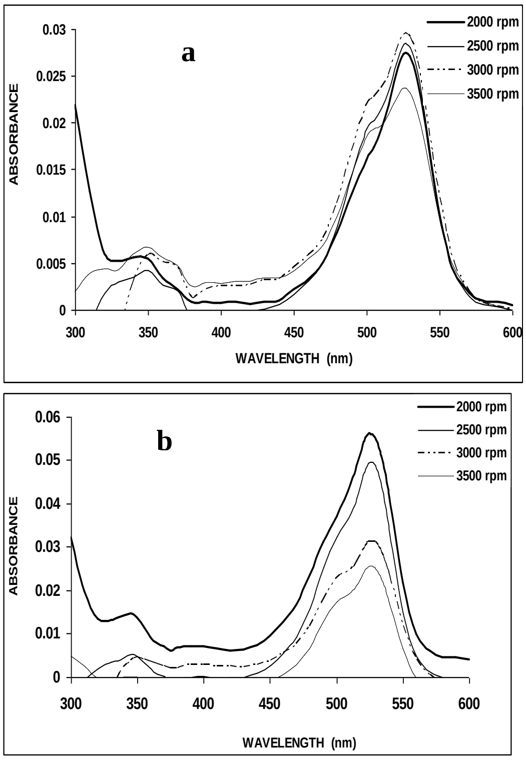


Fig. (4): Absorption spectra of R 6G film samples at 10 $^{-4}$ M; (a) one layer, (b) two layer

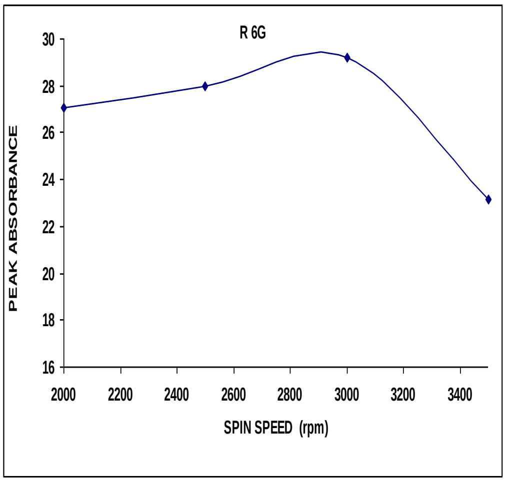


Fig.(5): peak of Absorbance via spinning speed: for Xerogel film sample R 6G

A set of R6G hybrid films were synthesized by spin coating, using the same deposition parameters (spinning speed and time), in order to study the effect of the densification on the optical properties.

An oven has been used to perform the densification process. The samples were placed into the oven at room temperature, and then heated up to the desired densification temperature at a constant rate ($\Delta T/\Delta t \approx 15\ ^{0}C/h$). After one hour at the selected temperature, the samples were cooled down to room temperature at the same rate. This procedure was followed in order to minimize surface stresses and possible film cracks.

In Figure (6), the absorption spectra of R6G spun films, before and after densification at 70 °C drying temperature, are shown.

It can be noticed that the absorption band (at 506 nm) related to the aggregation decreases after drying. On the contrary, the absorption band related to the monomer increases after drying. The apparent increase and the red shift of the monomeric absorption band (at 532 nm) is only an artifact due to the simultaneous decrease of the dimeric band.

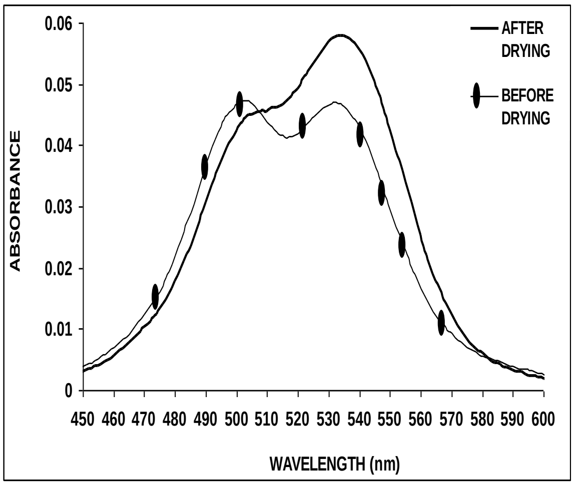


Fig. (6): The drying effect on R 6G spun films at concentration of 10^{-4} M.

Formaldehyde effect:

Figure (7) shows the effect of the formaldehyde additive in the Sol-Gel solution. The absorption spectrum of R 6G film at concentration of 10^{-4} M using formaldehyde recipe, has higher absorbance and being more narrow compared with normal recipe. This may be attributing to ability of formaldehyde to increase the surface tension of the Xerogel network during the spin process, hence the dye molecules become more relaxed, and the intermolecular processing may be reduced.

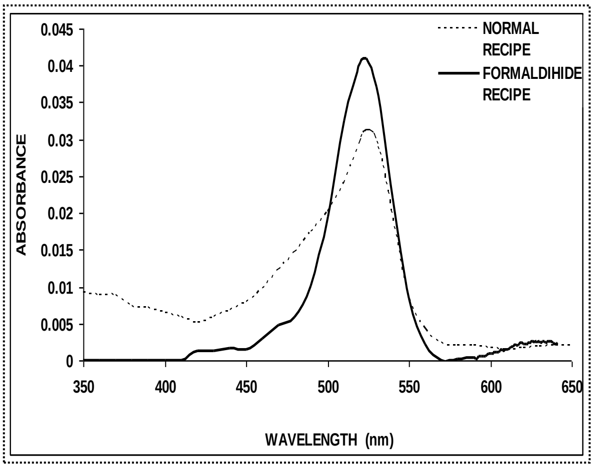
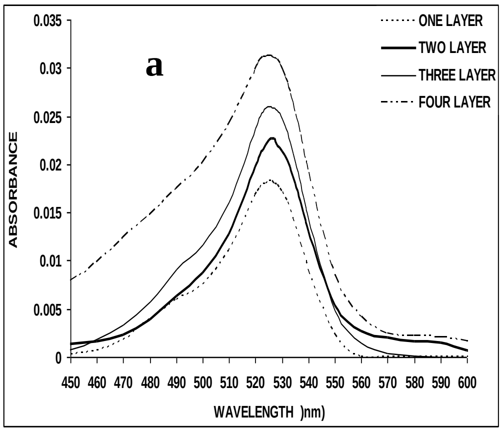


Fig. (7): The absorption spectra of four layer R 6G spun film, for normal and formaldehyde recipes, at dye concentration of 10^{-4} M.

Multilayer normal recipe:

Returning to Figures (4 a, b), one can see that larger ratio of the absorbance peak of the monomer to that of the dimer, as well as the higher absorbance in the two layer R 6G samples were obtained at 2000 rpm spinning speed. This speed has, therefore, been chosen for multilayer film preparation.

Figure (8-a) illustrates the absorption spectra of R6G multilayer film. From the figure one can see that the absorbance increased as the number of layers increased. This behavior is expected according to Beer- Lambert law, where the sample thickness increases with the increasing of the number of layers. In the normal recipe, the four layers film was neat and crack free, while the films that were spun for more than four layers the product often cracked. There was no variation in the peak absorption wavelength positions for the entire four layers and they were fixed on 528 nm.



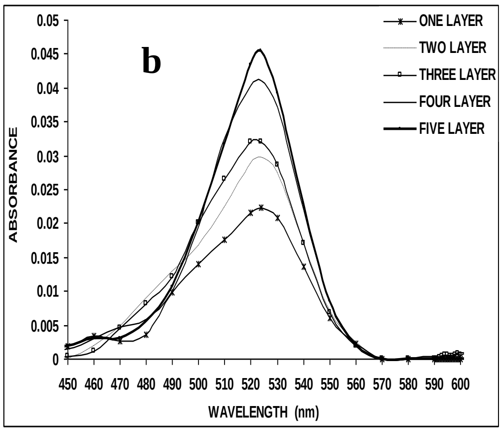


Fig.(8): Absorption spectra of multilayer R 6G spun film samples, at dye concentration of 10^{-3} M, synthesized by; (a) normal recipe , (b) formaldehyde recipe.

Multilayer formaldehyde recipe:

In the case of formaldehyde recipe, Figure (8-b), neat, optically clear and crack free five layers films had been achieved. Also the formaldehyde recipe samples have high absorbance compared with normal recipe samples. Also there was no variation in the peak absorption wavelength positions for the entire five layers and they were fixed at 525 nm. There was blue shift of the absorption peak wavelength in the formaldehyde samples with respect to the normal samples. This may be attributed to the similar reasons mentioned earlier.

Conclusion:

The increase of the concentration during the drying of the laser dye solution in the Sol-Gel processes must be taken into account when one chooses the starting concentration of the laser dye. The solid Xerogel matrices doped with dye increase the ability of preparation of high concentration samples and minimize the interactions with the adjacent dye molecules.

In the formaldehyde recipe, the Xerogel film absorption spectrum becomes more structured when the drying temperature increases from room temperature to 70 °C.

The absorbance peak of Xerogel films doped with R6G increases with the increase of the spinning speed and the ratio of the peak absorbance of the monomer to that of the dimer increases too. Also the absorption spectra at the lowest speed were almost structureless, while at higher speeds they become more structured. Also its absorption band at 516 nm, which is related to aggregation, decreases after drying. On the contrary, the absorption band related to the monomer increases after drying.

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