# Study of Spinning Speed, Multilayer Coating and Formaldehyde Effect on Preparation of Xerogel Film Doped with Laser Dyes

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Spin coating technique has been applied in this work to prepared Xerogel films doped with three laser dyes (Rhodamines R101, 6G and Coumarin 153). The solid host of laser dye modifies its spectroscopic properties with respect to the liquid host. During the spin coating process the dye molecules suffer due to variations in their environment. The effects of three parameters, the spinning speed, multilayer coating and formaldehyde addition are studied here.

# 1. Introduction

There are two main types of coating techniques, depending on the effect to be obtained and the material to be used: namely the gas phase vacuum and the wet coating techniques. The first one requires high temperature and is therefore expensive. 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, spray 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. As shown in Fig. 1, the spin coating process can be divided into four major stages:

- a. Deposition, 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, the second stage for covering or wetting the entire surface of the substrate with excess coating liquid;
- c. Spin-off, the third stage for removing the excess liquid from the entire surface of the substrate; and
- d. Evaporation of solvents, the last stage when the liquid solidifies due to the solvent evaporation.



Fig.1: The spin coating steps from (a) to (d).

African Physical Review (2009) 3: 0017

The two common methods of dispensing 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. The spinning speed is one of the most important factors in spin coating process. As the resin dries, the viscosity increases until the radial force of the spin process can no longer move significantly the resin over the surface. At this point, the film thickness will not decrease significantly with an increased spinning time. The acceleration of the substrate towards the final spinning speed can also influence the coated film properties, since the resin begins to dry [6].

# 2. Chemical material

The following materials were used: tetraethylorthosilicate (TEOS) (Purity 95%) was supplied by Ibn Sina state Co. and then redistilled twice in our laboratory; Ethanol was of Analytical grade (Purity 99.9%) supplied by Gainland Chemical Company, U.K.; Rhodamine 101 (molecular weight 591.06 gm/M Lc (6400)); Rhodamine 6G (molecular weight 479.02 gm/M Lc (5900)); and Coumarin 153 (molecular weight 309.29 gm/M, Lc (6400)), all supplied by Lambda physik [7]. Fig. 2 shows the chemical structure of these dyes [7].





Com 153

Fig.2: The chemical structure of the dye used [7].

# 2.1 Preparation of film samples

The Xerogel Film samples were prepared using Sol- Gel technique. Two recipes mentioned in the flowchart were tested and the laser dyes were dissolved in ethanol at concentration of  $5 \times 10^{-4}$ M. Both of these recipes, normal (routeno 1) and formaldehyde (routeno. 2) were used in this work (Fig. 3). The details of the preparation process using the Sol-Gel technique are mentioned elsewhere [8].

### 2.2 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 dyes have been produced using a diode-pumped solid state green laser as a light source of wavelength 531.5nm, CW output power of 10 mW with line width 2 nm and 2 mm beam diameter. The dye fluorescence emission was detected through a Jarrell ash monochromatic model 82-000. This unit is an Ebert scanning spectrometer of 0.5 meter focal length with eight speed electric drives and plane reflection grating of 1180 groove/mm. The detection unit is a photomultiplier PMT (type S666 Hamamatsu), which was connected to an X-Y/t recorder (SIEMENS) to record the output signal.

# 2.3 Measurement setup of film fluorescence

The laser beam was 2 mm in diameter, which is small compared to the substrate dimensions  $(20\times20 \text{ mm})$ . The number of molecules in the laser beam path that could possibly be excited is relatively small due thinness of the film. Therefore, the laser beam diameter and shape must be modified to increase the interaction of molecules with the laser light. This was achieved by using beam expander to increase the beam diameter and cylindrical lens to modify its shape from circular to linear.

The optical system design was done with the help of a special computer program, OPTICAD, which is used for optical system design. Fig. 4 illustrates the optical setup to get the effective illumination of the Xerogel doped dye film.



Fig.3: Preparation procedure flowchart for normal and formaldehyde recipes.

# 3. Xerogel film testing

At first, the speed effects on the optical properties of the products were studied, since 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) to produce films with the desirable properties.

Fig. 5a and Fig. 5b show the speed effect on the absorption spectra of Com. 153 film samples at  $5 \times 10^{-4}$  M, of one layer and two layers, respectively.

One can see from Fig. 5a that the peak absorbance goes up with an increase in the spinning speed (see also Fig. 9a). Also, there is an increase in the ratio of the peak absorbance of the monomer (at  $\lambda$ =425) and the dimer (at  $\lambda$ = 370) (see also Fig. 8). This behavior still dominates when the films were spun for two layers (Fig. 5b). One notices also that the absorption spectra at the lowest speed were almost without structure, while at higher speeds they became more structured.

Fig. 6a and Fig. 6b, respectively, show the speed effect on the absorption spectra of R 6G film

samples at 10<sup>-4</sup> M of one and two layers. This dye has neat and structured spectra for all spinning speeds. Fig. 6a, for one layer samples, shows that the peak absorbance increases as the spinning speed increases, reaching a maximum value at about 3000 rpm and then decreases (see Fig. 9b). In the case of two layers, the peak absorbance decreases monotonically as spinning speed increases. A similar behavior was noticed for the ratio of the peak absorbance of the monomer to that of the dimer (see Fig. 8).

Fig. 7a and Fig. 7b show the speed effect on the absorption spectra of R 101 film samples at  $10^{-4}$  M for one and two layers, respectively. The absorption spectra of R 101 samples for both one and two layers, as well as for all spinning speeds show relatively broad spectra. This may be attributed to the aggregation and dimer formation of R101 dye molecules inside the Xerogel film host as a result of the heavy molecular weight and the large size of the dye molecule (see Fig. 2), which yields non Newtonian liquid.



Fig. 4: Schematic diagram of the fluorescence spectrum setup.



Fig.5: Absorption spectra of Com. 153 film samples at  $10^4$  M for: (a) one layer (b) two layer.



Fig.6: Absorption spectra of R6G film samples at 10<sup>-4</sup> M for (a) one layer (b) two layer.



Fig.7: Absorption spectra of R101 film samples at  $10^{-4}$  M: (a) one layer (b) two layer.

There are no noticeable changes in the ratio of the peak absorbance of the monomer to that of the dimer for the entire spinning speeds; and there is a slight increase of peak absorbance with the increase of the spinning speed (see Fig. 8, Fig. 9c).

This study focuses upon R6G dye because of its high photochemical and photophysical stability and large absorption cross section [9].

A set of R 6G hybrid films were synthesized by spin coating to study the effect of the densification

on the optical properties using the same deposition parameters (spinning speed and time).

An oven has been used to perform the densification process. The samples were placed in the oven at room temperature and then heated to the desired densification temperature at a constant rate ( $\Delta T/\Delta t \approx 15$  °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.



Fig.8: Monomer to dimer peak absorbance ratio against the spinning speed.



Fig.9: Absorption spectra of Xerogel film samples: (a) Com.153, (b) R 6G and (c) R 101.

The absorption spectra of R 6G spun films, before and after densification at 70  $^{\circ}$ C drying temperature, are shown in Fig. 10.

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.

#### 3.1 Formaldehyde effect

Fig. 10 shows the effect of the formaldehyde additive in the Sol-Gel solution. The absorption spectrum of R 6G film at a concentration of  $10^{-4}$  M using formaldehyde recipe has higher absorbance and is narrower as compared to normal recipe. This may be attributed to the 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 intramolecular processing may be reduced.



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

# 3.2 Multilayer normal recipe

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

Fig. 11a illustrates the absorption spectra of R 6G multilayer film. One can see from the figure that the absorbance increases as the number of layers increases. This behavior is expected according to Beer- Lambert law, where the sample thickness increases with the increase of the number of layers.

In the normal recipe, the four layer 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 all four layer films fixed at 528 nm.

#### 3.3 Multilayer formaldehyde recipe

In case of formaldehyde recipe, see Fig. 11b 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 peak absorption wavelength in the formaldehyde samples with respect to the normal samples. This may be attributed to the similar reasons mentioned earlier.



Fig.11: Absorption spectra of multilayer R 6G spun film samples at dye concentration of  $10^{-4}$  M synthesized by: (a) normal recipe (b) formaldehyde recipe.

## 4. Conclusion

The increase of the concentration during the drying of the laser dye solutions 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 dyes 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  $^{\circ}$ C.

The peak absorbance of Xerogel films doped with R6G goes up with an increase of the spinning speed, as well as the ratio of the peak absorbance of the monomer to that of the dimer. The absorption spectra at the lowest speed were almost without structure, while at higher speeds they became more structured. Moreover, its absorption band at 516 nm, related to aggregation, decreases after drying. On the contrary, the absorption band related to the monomer, increases after drying.

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Received: 28 October, 2009 Accepted: 01 March, 2010