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Spectro-ellipsometric studies of activated sol-gel thin films to detect Cu²⁺ ions in aqueous solutions

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Abstract

Thickness, refractive index *n* and extinction coefficient *k* of eriochrome cyanine R (ECR) dye doped mesostructured silica film (ECRMSSF) dip-coated on silicon wafers without prior removal of surfactant have been determined in the visible range of the spectrum by spectroscopic-ellipsometry (SE). ECRMSSF was used as sensing detection layer of Cu^{2+} in aqueous solutions of known pH. The dependence of optical parameters on the pH range of the aqueous phase (pH = 6–8) was investigated. The detection reversibility of ECRMSSF was demonstrated. An electron paramagnetic resonance spectrum demonstrated the complexation of Cu^{2+} by the entrapped ECR.

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1. Introduction

Spectro-ellipsometry (SE) is a non-destructive technique well adapted to thin film characterisations [1–3]. Ellipsometry uses light of known polarisation incident on a surface under study and detects the polarisation state of the reflected light. Incident light is usually linearly polarised and reflected light has elliptical polarisation, where coordinates of incoming field vector E are the p- and s-polarisations. Ellipsometry measures changes of the light polarisation by the reflection at an interface. The measured values are related to the ratio of Fresnel reflection coefficient r_p and r_s for p and s-polarisation light, respectively:

$$r_p/r_s = \tan \psi e^{i\Delta},\tag{1}$$

where r_p and r_s are the reflection coefficients of the electric field on the film surface with polarisation parallel and perpendicular to the plane of incidence, respectively. From Eq. (1), the ratio is seen to be a complex number, thus it

contains "phase" information contained in Δ , which makes the measurements very sensitive. The advantage of the ellipsometric measurement is the ability to obtain the real part and the imaginary part of dielectric function simultaneously; therefore, the value of the complex refractive index N(N = n + ik) as a function of wavelength can also be obtained. The real part n of refractive index generally relates to dispersion, while the imaginary part kprovides a measure of the dissipative rate of the wave in the medium [3]. Absorption coefficient (α) can be deduced from the complex dielectric function (ε) using the following equation: $\alpha = 4\pi k/\lambda = (2\pi/\lambda n)\varepsilon_2$, where $\varepsilon_1 = n^2 - k^2$, $\varepsilon_2 =$ 2nk and λ is the wavelength (nm). The ε_1 and ε_2 format are most appropriate when discussing the physics. The *n* and *k* format are used extensively in engineering applications [2]. So, SE measurements can be used to confirm absorption investigations and more importantly, give particular access to optical parameters and thickness.

The goal of this work is to confirm, by SE measurements, the previous spectrophotometric results of eriochrome cyanine R (ECR) dye doped mesostructured silica Cu^{2+} detection (ECRMSSF- Cu^{2+}) [4]. Results of cited studies showed that ECR incorporated in mesostructured silica

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matrix without prior removal of surfactant is sensitive with adjusted pH (ECRMSSF-pH) to Cu^{2+} (ECRMSSF-pH- Cu^{2+}). Cationic surfactant cetyltrimetylammonium bromide (CTAB) seems to favour the trapping of dye in host matrix limiting at the same time the leaching of the dye. The ECR molecule, frequently used in chemical analysis as an indicator for complexometry and particularly for Cu^{2+} ion detection [5–12], has two carboxylic groups, one hydroxyl, one carbonyl and one sulphonic group which ensure compatibility with polar solvents that are commonly used in sol–gel synthesis [10].



Sol-gel processing is a versatile procedure for making advanced materials. The recent discovery of mesostructured silica formed by the cooperative self assembly of silicates and surfactants has opened up a new range of possibilities. The highly porous nature of these materials makes them excellent hosts for sensing molecules, since the species to be sensed can easily diffuse towards the sensing centre. Sol-gel technology has proved very useful to prepare pH detectors [13–15], electrochemical sensors [16,17] and especially optical sensors [4,18,19] for the detection of the metal ions in aqueous solutions. In a typical sol-gel process, the precursor is subjected to a series of hydrolysis and polymerisation reaction to form a

For this study, the sol was prepared via acidic hydrolysis condensation of tetraethoxysilane (TEOS) in the presence of CTAB as the structure-directing agent. The surfactant was not removed and has been exploited for the lowtemperature synthesis of optical materials and it acts here as a barrier to limit the leaching of the dye.

colloidal suspension, or sol.

ECR entrapped in sol-gel composites displays a selectivity for complexing metal ions which is different from that of the dye in solution [7]. In a recent paper, Wright and Higginson [12] examine the effects of pH on a gel prepared by sol-gel route using various values of the water-alkoxide (tetramethoxysilane) ratio and showed that ECR sensitivity increases on incorporation of 10% methyltriethoxysilane. With the aim of detecting scandium (Sc(III)), Park and Cha [8] conclude that the complex between ECR and Sc(III) in the presence of surfactant (CTAB) is very stable and more sensitive than in its absence. They interpret this mechanism by the formation of Sc(III)–ECR–CTAB ternary complex. Previous work [4] using optical absorption performance of ECR to detect Cu^{2+} after exposure for various time to a pH 8 buffered

solution containing 5 mmol/l of Cu²⁺ at $\lambda = 580$ nm (Fig. 5a) confirmed that ECR is well entrapped in the mesostructured film with limited leaching.

2. Experimental details

A prehydrolysed solution was prepared by refluxing for 1 h an ethanolic solution containing TEOS, deionised water and hydrochloric acid in the following molar ratio: 1 TEOS: 3 EtOH. 5×10^{-5} HCl: 1 H₂O. Then. CTAB was dissolved in ethanol and added to the prehydrolysed solution together with an additional amount of water and HCl. Typically, the final molar ratio was 1 TEOS: 20 EtOH: 0.004 HCl: 5 H₂O: 0.1 CTAB. The pH of sol was around 2. The dye ECR (1 mmol/l of sol) was introduced in the sol and left under stirring for an hour. The resulting solution had a red coloration and the pH of mixture was around 4 and this pH accelerates solidification of the sol (we can conclude that ECR acts as a basic indicator when it is added to the described sol and thus can be explained by the hydroxyl group of ECR). Stabilisation of the sol was achieved by bringing back pH of the sol to 2 by adding one drop of 2 M HCl. Sol has now a yellow coloration. The doped and un-doped sols were then stirred for 4 days at room temperature and a series of films were then dipcoated on silicon wafers. Films were deposited at a velocity of 3.1 mm/s at room temperature and left in an oven during one night at 60 °C followed by 4 h at 130 °C.

With the aim of confirming the metal-complexing dye ECR to Cu^{2+} , an electron paramagnetic resonance (EPR) Cu^{2+} test was performed using a Bruker spectrometer (v = 9.241 GHz) at room temperature. An amount of sol was left at room temperature one night and the gel was then dried at 130 °C and powdered. ECRMSS powder was suspended in a Cu^{2+} solution (1 mmol/l) stabilised at pH = 8 and left under stirring for an hour and then filtered and finally extensively rinsed with water and dried. The powder has now a blue coloration.

3. Results and discussion

Ellipsometric measurements were performed in the visible range (350-650 nm) for different incident angles 65°, 70° and 75°. Film thickness of dip-coated silicon wafers (ECRMSSF) was around 180 nm. For un-doped mesostructured silica film (MSSF), the refractive index versus wavelength is shown in Fig. 1. Refractive index *n* decreases from n = 1.50 (350 nm) to n = 1.47 (650 nm) which verifies the Cauchy equation in the absence of absorption (k = 0):

$$n(\lambda) = A + (B/\lambda^2) + (C/\lambda^4), \tag{2}$$

where the three parameters in the dispersion model are A, B and C, and λ is the wavelength. Refractive index of MSSF seems greater than pure silica (n = 1.457) in the visible range. This could be due to the presence of CTAB.



Fig. 1. Refractive index *n* of mesostructured silica film (MSSF) versus wavelength showing monotonic decrease. Relative to pure silica (*n* = 1.458 at $\lambda = 600$ nm), the surfactant seems to increase the refractive index.



Fig. 2. Refractive index $n(\lambda)$ of initial (before exposure to pH) ECR dye doped mesostructured silica film (ECRMSSF). We note the appearance of a dispersion peak at $\lambda = 543$ nm certainly due to the presence of the dye.

The ellipsometric spectra of refractive index n and the extinction coefficient k of ECRMSSF before exposing to pH are shown in Figs. 2 and 3, respectively. Refractive index n shows a peak at 543 nm (n = 1.475) certainly due to the presence of dye. The corresponding extinction coefficient k shows a peak at 531 nm.

The response of ECRMSSF versus pH (ECRMSSF-pH) of carrier solutions (distilled water) in the range pH = 6-9 was performed using acetic acid and ammonia to adjust the



Fig. 3. Extinction coefficient k versus wavelength (nm) of ECRMSSF (as dip-coated) with a peak centred at 531 nm.

carrier solutions to the desired pH. Before each ellipsometric measurement, the films were dried. The SE results relative to refractive index *n* and extinction coefficients *k* versus wavelength were plotted in Figs. 4 and 5, respectively, including those of ECRMSSF and MSS films. In the visible range (350–650 nm), pH effect (when pH of carrier solution increase from 6 to 9) decreases refractive index of ECRMSSF and shifts the extinction coefficient maximum from 532 to 432 nm. The absorbance at $\lambda =$ 432 nm increases as pH decreases. These results confirm the previous spectrophotometer investigations [4] and are in agreement with the work of Sommerdijk et al. [7] and Villegas et al. [10].

In the following experiments, pH = 8 was retained to test the capability of ECRMSSF to detect Cu²⁺. After exposure to pH = 8, the film was successively immersed in 1 mmol/l of Cu²⁺ solution for 15 min, rinsed, dried and then tested. Results are shown in Fig. 6. Absorption was centred on 591 nm when the film was exposed to Cu^{2+} solution. We can summarise the behaviour of the film with respect to wavelength by the following absorption maxima: initial film (531 nm), exposed to pH = 8 (432 nm) and exposed to 1 mmol/l of Cu^{2+} (591 nm). A previous absorption investigation [4] gives a peak centred at 582 nm when the dip-coated film was stabilised at pH = 8and exposed to Cu²⁺ solution. The two methods (spectrophotometric and spectro-ellipsometric) seem confirmed the ECR complexing metal ion Cu^{2+} around 590 nm. The advantages that can actually be gained using the SE method were the access to optical parameters as extinction coefficient $k(\lambda)$ (which related to absorption coefficient) and thickness.



Fig. 4. Comparison between refractive index $n(\lambda)$ of un-doped mesostructured silica film (MSSF), ECR dye doped mesostructured silica film as dip-coated (ECRMSSF) and ECRMSSF exposed to different pH: (a) MSSF, (b) ECRMSSF (initial film before exposure to pH effect), (c) ECRMSSF-pH = 9, (d) ECRMSSF-pH = 8, (e) ECRMSSF-pH = 7 and (f) ECRMSSF-pH = 6.



Fig. 5. Comparison between extinction coefficient $k(\lambda)$ of ECRMSSF and ECRMSSF exposed to different pH in the range pH = 6–9.

To test reversibility of detection, the same film was immersed in acidic solution (2 M HCl) for 1 min (placing the film in 2 M HCl displaced the copper ions and regenerated the reagent), stabilised at pH = 8 (Fig. 7)



Fig. 6. Extinction coefficient $k(\lambda)$ of ECRMSSF, ECRMSSF exposed to different pH and ECRMSSF stabilised at pH = 8 (ECRMSSF-pH = 8) and then exposed to 1 mmol/l of Cu²⁺ solution for 10 min (ECRMSSF-pH = 8-Cu).



Fig. 7. Regeneration of film: extinction coefficient *k* versus wavelength of: (a) ECRMSSF stabilised at pH = 8 and then (b) successively exposed to 1 mmol/l of Cu^{2+} solution for10 min, followed by exposure to 2 M HCl (placing the film in 2 M HCl displaced the copper ions and regenerated the reagent) and finally stabilised at pH = 8; regeneration of film was so proved.

and again immersed in 1 mmol/l of Cu^{2+} solution for 20 min, rinsed, dried and then tested (Fig. 8). Reversibility is proved with about 10 nm shift. Increase of peak intensity was due to increased diffusion of Cu^{2+} ions to complexing sites deeper within the bulk of the film in the greater

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Fig. 8. Reversibility of detection: extinction coefficient *k* versus wavelength of: (a) ECRMSSF-pH = 8-Cu²⁺ and (b) the same film of (a) was used after ellipsometric test for regeneration (by exposition to 2M HCl solution) followed by stabilisation to pH 8 and finally re-exposed to Cu²⁺ solution.



Fig. 9. Comparison between refractive indexes $n(\lambda)$ of: (a) ECRMSSF, (b) ECRMSSF-pH = 8 and (c) ECRMSSF-pH = 8-Cu²⁺.

exposure time to the Cu^{2+} solution. Refractive index *n* in this case is illustrated by Fig. 9. We note a dispersion peak at 618 nm when film was exposed to Cu^{2+} .

In this study, ECR seems well immobilised in the matrix. In fact, previous work using optical absorbance of ECR to detect Cu^{2+} as a function of exposure time to a pH 8 buffered solution containing 5 mmol/l of Cu^{2+} showed an



Fig. 10. EPR test.

absorption increase not fully equilibrated after 5 min exposure. This result is in good agreement with the work of Sommerdijk [7] and Wright and Higginson [12] using sol-gel-entrapped ECR. SE method used in the actual work seems well adapted to dye-doped mesostructured thin films absorption-dispersion investigations with a great sensitivity.

The EPR spectra were recorded on a Bruker spectrometer at room temperature operating at 9.241 GHz and 100 kHz field modulation. The results are given in Fig. 10 which showed a well-resolved copper hyperfine features and narrow EPR signals. The spectrum is characterised by the parameters

$$g = hv/\beta_e B_{res}$$
 (with $B_{res} \approx 3170$ Gauss) ≈ 2.08

$$\frac{|a|}{\beta_e} = 2760 - 2620 = 140$$
 Gauss.

The EPR spectrum of Cu-ECR-MSS is typical of Cu^{2+} [20,21].

4. Conclusion

The ellipsometric spectra in the visible range of ECR dye doped mesostructured silica sol dip-coated on silicon wafers were studied for different incident angles 65° , 70° and 75° by spectroscopic ellipsometry. The refractive index $n(\lambda)$, extinction coefficient $k(\lambda)$ and thickness of the films have been obtained. Analysis of dye-doped sol-gel films shows the presence of two phenomena which are dispersion and dissipation related, respectively, by the refractive index n and the extinction coefficient k. The pH range (6–8) seems to be the optimal absorption pH. Detection of Cu²⁺ ions by sol-gel dip-coated thin films on silicon wafers and powder was examined, respectively, by spectro-ellipsometric measurements and RPE tests which confirm the previous spectrophometric studies and evanescent optical fibre wave sensing of the detection capability of ECR activated mesostructured silica sol-gel matrix. The aims of previous [4] and actual studies using spectroscopic investigations constitute a step to enhance sensitivity of optical fibre Cu^{2+} continuous sensing based on optical evanescent field and activated sol-gel detection layer. For enhancing sensor sensitivity, the future investigations are planned to explore the structure phase and pore size distributions of dip-coated films, particularly the effect of the mole ratio of dye molecule to surfactant [22].

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