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Quadratic nonlinear optics to assess the morphology of riboflavin doped chitosan for eco-friendly lithography

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ABSTRACT

We report the use of the Second Harmonic Generation response from a riboflavin doped chitosan film as a characterization method of the film morphology. This film is of particular interest in the development of new and bio-sourced material for eco-friendly UV lithography. The method allows us to determine how riboflavin is distributed as a function of film depth in the sample. This possibility is of importance in order to have a better understanding of the riboflavin influence in chitosan films during the lithography process. On the contrary, linear optical techniques provide no information beyond the mere confirmation of the riboflavin presence.

1. Introduction

Photolithography can nowadays achieve designs with high 2D spatial resolution for a wealth of industrial applications, notably in the field of nanoelectronics. This possibility results from the technical developments realized over the years in nanofabrication in the decrease in wavelength or the development and optimization of materials (masks, resists) and devices (lens, wavelength sources, exposure tools …) for each technological node [1].

Photolithography is based on the use of photoresists generally composed of a polymer, a solvent, a photoactive component as a photoacid generator, a quencher and different additives. This polymer solution is coated on the substrate leading to a thin film then patterned through photolithography. After development, it forms a temporary mask that protects selected areas of the underlying substrate allowing for the micro/nanopatterning (by etching or depositing matter locally) of the substrates for the fabrication of the devices. However, with a growing concern on environmental and health issues, new green photoresists are required. In this context, chitosan as a natural polymer, sub-product of the chitin shells of shrimps and other crustaceans, offers interesting possibilities. Its doping with riboflavin, a natural dye, seems promising.

Chitosan is a polysaccharide constituted of D-glucosamine and *N*-acetyl-D-glucosamine units linked by a β- (1 → 4) glycosidic bond (Fig. 1). This compound is naturally present in insects and microorganisms but can be also industrially prepared from chitin by treatment with an alkaline solution [2]. Chitin is the second most abundant biopolymer on Earth. It is extracted from wastes of seafood industry like crustacean shells from crabs and shrimps in particular. Chitosan is nontoxic, biocompatible and biodegradable At acidic pH, chitosan is soluble in aqueous solutions. Riboflavin or vitamin B_2 (Fig. 1) is a natural and hydrosoluble dye present in fruits, vegetables and animals [3]. It is known for its photosensitivity and used as a photodegradation agent of organic pollutants in water treatment [4]. Riboflavin-doped photosensitive chitosan films can be used for an eco-friendly and water-developable photolithography.

In photolithography, the polymer solution is spin-coated on a substrate prior to illumination. Therefore, novel characterization methods need to be proposed to determine the physical properties of the polymer thin film in view of the targeted eco-friendly lithography. In particular, the morphology of the film must be determined since the riboflavin distribution within the film is of utmost importance. Indeed, as the solvent is evaporated from the film, the solubility limit of riboflavin (around 2×10^{-4} mol L^{-1}) may be reached leading to phase

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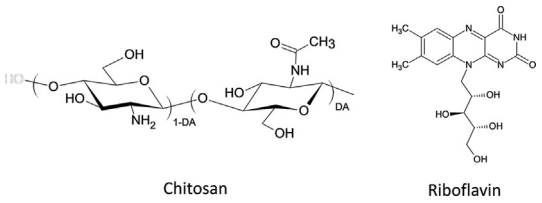

Fig. 1. Chemical structures of chitosan and riboflavin.

segregation whereas a homogeneous distribution is desired. Linear optical methods like UV–visible absorption and fluorescence spectroscopies are among the simplest methods and indeed provide valuable information. Chitosan, although presenting a weak fluorescence, has no prominent features in the visible part of the spectrum as opposed to riboflavin which possesses both strong absorption and fluorescence bands. Yet, linear optical methods are known to lack longitudinal resolution along the direction of propagation and are therefore of limited use when dopant depth profiles are sought at micrometer resolution or better.

In order to improve the longitudinal resolution of the optical characterization, we propose in this work to use different complementary nonlinear optical methods. First, we have applied the two photon excited fluorescence (TPEF) method which permits to obtain a three-dimensional resolution owing to the multiphoton excitation process [5–7]. Indeed, because two photons are simultaneously required to achieve material excitation, the nonlinear optical process can only occur at the focus of the beam [8]. Thus, with a typical focal volume of 10 μm^3, a depth resolution of few micrometers in the plane perpendicular to the propagation direction can be achieved. However, the linear and nonlinear methods have a similar resolution limited by diffraction and are not so well suited to investigate the film interfaces. Therefore, we propose to also perform Second Harmonic Generation (SHG) measurements at the air-film interface [9]. The SHG process whereby two photons at the fundamental frequency are converted into one photon at the harmonic frequency, is highly sensitive to the symmetry of the material and in particular, is forbidden in media with inversion symmetry within the dipole approximation, that is within the volume of the film. Hence, the method is inherently surface sensitive and should allow us to go further in assessing any presence or accumulation of riboflavin at the air-film interface. The surface sensitivity is here determined by the extent of the centrosymmetry breaking into the film. The interface is a region where the centrosymmetry is broken whereas the volume is centrosymmetric by nature. Similarly to liquids, this interface region where the centrosymmetry is broken should not exceed a few molecular layers, i.e. should be of the order of a nanometer. With the combination of TPEF and SHS, to determine the riboflavin distribution in the film volume, and SHG, to determine its presence or absence at the film interfaces, one can thus retrieve a full picture of the riboflavin spatial distribution. In fact, after the first few atomic or molecular layers, any centrosymmetric media will exhibit no coherent SHG signal. Only the symmetry breaking due a media change at the surface, can give any signal for a centrosymmetric media.

From the molecular structure of riboflavin which contains delocalized electrons in an asymmetric environment (Fig. 1), we can expect that the molecule exhibits a significant first hyperpolarizability, namely its cross-section for SHG, and thus a significant second harmonic intensity. The first hyperpolarizability of a molecular compound can be determined by the Second Harmonic Scattering (SHS) method [10–12], also referred as incoherent SHG. In this case, the harmonic light results from the scattering by a molecular suspension in a liquid due to orientation fluctuations. In this paper, we therefore report the SHG response from a riboflavin doped chitosan film deposited on a silicon substrate supporting a 200 nm silica layer. We first determined the film linear optical properties and the riboflavin first hyperpolarizability when dispersed in bulk solution using the SHS technique. Then, the TPEF and SHG intensities of riboflavin in thin chitosan films were recorded. The 2D spatial distribution of the molecules in the film was characterized by nonlinear imaging. Finally, surface SHG measurements were performed in order to confirm the absence of riboflavin at the air-film interface.

2. Experimental section

2.1. Chemistry

Riboflavin was purchased from Sigma-Aldrich (> 98%). Chitosan was purchased from Mahtani Chitosan PVT, Ltd (India) and was characterized by its molecular weight and its degree of acetylation (DA) corresponding to the number of *N*-acetyl-D-glucosamine units along a chain of chitosan. In our case, chitosan was extracted from squid pens with a DA of 2% and a molar mass of 569.9 kg mol^{-1}.

A riboflavin solution concentrated at 2.2×10^{-4} mol L^{-1} in deionized water (ultra-pure, 18 MΩ cm) was prepared. Chitosan was dissolved in this solution at a concentration of 0.9% (w/v). To enable its total dissolution, acetic acid (Fluka Analytical, glacial acetic acid) was added at a final concentration of 0.05 mol L^{-1}. Riboflavin doped chitosan films were realized by spin-coating (5000 rd. min^{-1}, 3000 rd. s^{-2} during 30 s) on n-doped (100) oriented Si substrates with a 200 nm thick SiO_2 layer deposited by plasma enhanced chemical vapor deposition (PECVD). After spin-coating, the resulting film was heated at 100 °C for 1 min. The riboflavin-doped chitosan film thickness was 180 nm ± 5 nm. Film thickness was measured by ellipsometry with a spectroscopic ellipsometer UVISEL ™ from Horiba using the classical formula dispersion as modelled in the Horiba software. The model was adapted to chitosan by adjusting the refractive index between 1.5 and 1.6 and the extinction coefficient to 0 at 630 nm following Nosal et al. [13].

2.2. Exposure

Films were exposed to UV radiations through a photomask constituted of open zones (lines of 60 μm) in quartz and dark zones (squares of 440 μm × 440 μm) in chromium-iron oxide. Exposure was realized during 1 min on a MBJB4 UV SUSS Micro Tec UV lamp at 365 nm, 405 nm and 435 nm with a power density of 20 mW cm^{-2} at 405 nm and a lamp power of 200 W. Patterns were revealed in the riboflavin-doped chitosan films after development in deionized water for 60 s. Non exposed films were stored in clean room in the dark after preparation [14].

2.3. Linear optics

Ultraviolet–Visible absorption spectra were collected in a quartz cell with 1 cm path length using a double beam UV mc2 SAFAS spectrometer. One-photon excited fluorescence spectra were performed with a FLS920 fluorimeter from Edinburgh Photonics using quartz cells with 1 cm path length. A 450 W continuous xenon arc lamp was used as an excitation source.

2.4. Nonlinear optics

The nonlinear imaging experimental setup was based on a frequency doubled femtosecond Er-doped fiber laser source (Menlo Lasers, C-Fiber 780). The laser provided pulses with a duration of about 100 fs at a repetition rate of 100 MHz. The fundamental wavelength was set at 780 nm (spectral width of 13 nm) and an average power of about 65 mW was measured at the laser exit. The light beam was focused by a standard microscope objective (magnification ×20, NA 0.75) mounted onto a microscope stand (Nikon Eclipse TE2000-U with 3D positioning in inverted geometry) holding the sample. Galvanometric mirrors allowed for the beam to be swept to acquire non-linear images of various