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SFM and EFM Studies on a Clay-Based Dielectric Nanocomposite

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A Laponite clay-based lithium iodate nanocomposite has been synthesized for non-linear optical applications. The surface morphology of dip-coated optical waveguides were analysed by Scanning Force Microscopy (SFM) techniques. Individual Laponite particles were first imaged by using Intermittent-Contact Atomic Force Microscopy on pure Laponite layers. Electrostatic Force Microscopy was then used on nanocomposite waveguides in order to obtain a “chemical contrast” of sample surface. The strong electrical contrast observed was attributed to sample topography and not to the different properties of each nanocomposite constituent. Finally, in ambient conditions, dip-coated layers were also shown to be sensitive to humidity which leads to the occurrence of surface lithium iodate crystals with sub-micrometer size.

Keywords Non-linear optical waveguides; Laponite; lithium iodate; Electrostatic Force Microscopy

PACS: 42.65.Ky; 42.65.Wi; 07.79.Lh; 81.07.Bc

1. Introduction

The α form of lithium iodate (α-LiIO₃) is a polar non-ferroelectric material known for its large transparency range and high non-linear coefficients. Elaboration of planar optical waveguides on monocrystalline substrates (grown from aqueous solution), by ion exchange or implantation techniques, have been already demonstrated [1, 2]. Potential applications are however limited by such expensive processes as well as the small amount of luminescent ions that can be incorporated during the growth of single crystal. A recent alternative consists in doping an amorphous matrix with noncentrosymmetric nanocrystals.

As an example, we developed a clay-based nanocomposite by adding LiIO₃ into a Laponite suspension. First results on linear and non-linear optical properties of Laponite/LiIO₃ dip-coated waveguides are presented elsewhere [3, 4]. Attenuation of waveguides is about 4dB/cm and an effective non-linear coefficient of ∼1.5 pm/V has been measured. It is also shown that after drying and heat-treatment between 150 and 210°C, the...
structure of Laponite films naturally orientates nanocrystals with the x-axis perpendicular to the plane of the layer.

Here, Intermittent-Contact Atomic Force Microscopy (IC-AFM) and Electrostatic Force Microscopy (EFM) are used to further characterise the surface arrangement of Laponite particles and lithium iodate nanocrystals. Ageing of nanocomposite waveguides in ambient conditions is first studied in IC-AFM and dark field microscopy (light is scattered by surface objects). The electrical contrast evidenced by EFM investigations is then discussed.

2. Experimental

The Laponite JS, provided by Rockwood Specialties Inc., is a synthetic trioctahedral hectoritic clay of chemical composition \((\text{Si}_{8}(\text{Mg}_{5.5}\text{Li}_{0.4})\text{H}_{2}\text{O}_{24}\text{Na}_{0.7})\). Individual particles are disk-shaped crystals, \(\sim 25\) nm in diameter and \(\sim 1\) nm in width [5]. For thin films elaboration, a precursor solution is prepared at room temperature by dispersing 3 wt.% of Laponite powder in distilled water under strong agitation. A lithium iodate aqueous solution is then added to the clear colloidal suspension in order to get a LiIO\(_3\)/Laponite volume ratio ranging from 10% to 60%. According to the withdrawal velocity and the viscosity of the sol, the thickness of dip-coated layers ranges from 200 nm to 3 \(\mu\)m. After drying at 100°C, the layer is annealed in the temperature range 150–210°C in order to cause nucleation of LiIO\(_3\).

Optical characterisations are performed on a ZEISS metallographic microscope and the structure of composite films on a Philips \(\theta–2\theta\) X-ray diffractometer with the Cu(K\(_\alpha\)) radiation. IC-AFM and EFM experiments are carried out in ambient conditions with an Autoprobe CP research instrument (Veeco) operated in intermittent-contact mode. Amplitude modulation (oscillation amplitude is about 50–100 nm and the set-point chosen to be in the attractive regime) is used to maintain a constant sample-probe distance and to obtain sample topography. In our set-up, the “lift mode” is not implemented so that topography and EFM data are recorded simultaneously. Electrostatic Force Microscopy measures the long range electrostatic interaction between a sample deposited on a conductive substrate (gold-coated glass substrate or silicon wafer in our case) and an AFM tip. When a variable dc voltage \(V_{dc}\) and an ac voltage \(V_{ac}\sin(\omega t)\) are applied, forces experienced by the tip include a coulombic term and a capacitive one [6–8]:

\[
F = \frac{Q_s Q_t}{4\pi \varepsilon_0 z^2} + \frac{1}{2} \frac{dC}{dz} (V_{dc} + V_{ac} \sin(\omega t) + \varphi)^2
\]

\(Q_s\) represents static charges on the dielectric sample surface, \(Q_t\) the charge induced on the tip, \(z\) the vertical tip-surface separation and \(C\) the effective capacitance of the tip-substrate system. \(\varepsilon_0\) is the vacuum permittivity and \(\varphi\) the contact potential difference between the tip and the substrate. Standard lock-in detection techniques are used to record the \(\omega\) and \(2\omega\) components of the electric force given by:

\[
F_{\omega} = \left( - \frac{Q_s C}{4\pi \varepsilon_0 z^2} + \frac{\partial C}{\partial z} (V_{dc} + \varphi) \right) V_{ac}
\]

\[
F_{2\omega} = \frac{1}{4} \frac{\partial C}{\partial z} V_{ac}^2
\]
3. Structural Characterisation

X-Ray Diffraction (XRD) diagrams of pure Laponite layers indicate a large parallel orientation of Laponite particles on the substrate [9] as it was confirmed by IC-AFM (Fig. 1). Due to the AFM tip radius (∼15 nm), the apparent width of individual particle is measured at about 40–50 nm which is in good agreement with the dimensions of Laponite single particles. During annealing, the water localised in the inter-particle spaces evaporates inducing particle aggregation and densification of the layer.

For a layer containing 55 vol.% of LiIO₃, there is no evidence of lithium iodate crystallisation before annealing but after a 1 h heat treatment at 210°C the [100] and [101] lithium iodate peaks are observed (Fig. 2). From the widening of the [100] peak and according to Sherrer’s formula, the nanocrystals size perpendicular to the layer has been estimated to be in the range 10–50 nm. The predominance of [100] peak is characteristic of a natural orientation of nanocrystals with the c axis perpendicular to the surface, i.e., c axis in the layer plane. This is confirmed by the polarized optical microscopy image in Fig. 3 where naturally oriented domains, composed of self-organised nanocrystals, are visible. Maltese crosses are attributed to the birefringence of LiIO₃ nanocrystals. Nanocrystals grow from nucleation centres with c axis in radial directions.

On the other hand, if Laponite particles and LiIO₃ nanocrystals orientation have been determined, less is known about the size of nanocrystals in the layer plane as well as the sample morphology (surface roughness should be as small as possible for optical waveguides).

4. Ageing of Nanocomposite Waveguides

In this section, a special attention is paid to the surface roughness of nanocomposite dip-coated films. So far, no systematic study was done to investigate the ageing of optical
waveguides under specific humidity and temperature conditions. However the sequence of IC-AFM images in Fig. 4 clearly indicates an increase in the sample roughness for an optical waveguide stored in ambient conditions. Only Laponite particles are observable in Fig. 4a whereas larger structures appear after a period of 14 days. Actually, two types of structure can be observed in Fig. 4c. The smallest particles have an apparent width of about 50–60 nm (line 1, distance between cursors “A”) and correspond to Laponite particles whereas large structures (line 2, distance between cursors “A” ∼300–500 nm) are attributed to LiIO₃. In some cases, these large structures appear as hexagonal needles, a characteristic feature of LiIO₃ crystals.

The growing of surface lithium iodate crystals with micrometer size may be related to the swelling properties of Laponite films [10]. Ambient humidity may dissolve LiIO₃ nanocrystals and subsequent surface crystallisation would lead to the observed topography. Dark field microscopy images (Fig. 4 d–e) confirm that such altered surfaces are not suitable

Figure 2. X-Ray Diffraction pattern of a naturally oriented layer with 55 vol.% of LiIO₃.

Figure 3. Polarized light microscopy image of a naturally oriented layer with 55 vol.% of LiIO₃ after annealing at 210°C. LiIO₃ nanocrystals grow from nucleation centres with c axis in radial directions.
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Figure 4. (a–c) Sequence of IC-AFM images of a sample with 55 vol.% of LiIO₃. (a) time = d₀, scan size 1×1 µm², grey scale 20 nm, (b) time = d₀ + 7 days, scan size 2×2 µm², grey scale 20 nm, (c) time = d₀ + 14 days, scan size 2×2 µm², grey scale 80 nm. Typical size of large and small structures are given in the text. (d) (resp. (e)) Dark field microscopy image associated with (a) (resp. (c)).

5. Interpretation of EFM Signals

It is worth noting that both contact-mode AFM and phase imaging are not suitable to obtain detailed topography measurements and any chemical contrast (results not shown).

Sample topography, F₀ and F₂₀ images of a layer doped with 50 vol.% of LiIO₃ are depicted in Fig. 5. Note that this sample was kept in ambient conditions so that the white bumps in the surface morphology are attributed to the occurrence of LiIO₃ crystals. These crystals, that can be easily distinguished from Laponite particles, appear with a black contrast in the F₂₀ image and are related to a change in the capacitive term ∂C/∂z (see Eq. (2)). To measure the coulombic interaction associated with surface static charges, a spectroscopic study was performed by measuring the amplitude of F₀ versus the applied dc voltage (Fig. 5c). In the whole range of applied voltage, the F₀ signal measured directly on Laponite particles is higher than for LiIO₃ crystals. It is found that both signal nullify at Vᵋ = 0.15 Volt (this dc bias corresponds to the contact potential difference between...
Figure 5. (a) Sample topography (scan size 2×2 µm², grey scale 70 nm) and (b) simultaneously acquired $F_{2\omega}$ image where a topography-related contrast is observable (grey scale = 2 V). (c) EFM spectroscopy on Laponite particles (solid symbols) and surface LiIO₃ crystals (open symbols), $F_{\omega}$ nullifies at $V_{dc} = -0.15$ V. (d) $F_{\omega}$ image (same area as (a)) for which no contrast is detectable at $V_{dc} = -0.15$ V (grey scale = 2 V).

The gold substrate and the AFM tip) for which no electrical contrast is detectable in the corresponding $F_{\omega}$ image (Fig. 5d). It is therefore concluded that the electrical contrast arises only from the capacitive term $\partial C/\partial z$. $F_{\omega}$ and $F_{2\omega}$ images have similar topography-related contrast when $V_{dc} \neq 0.15$ Volt. Actually the same conclusion can be found in references [11] and [12] where the reduction in the tip-sample capacitance is explained as a change in the sample topography. The capacitance is weaker when the tip is scanned over a bump rather than a flat surface.

This led us to the following conclusions. First, we were not able, though it was expected, to image the surface arrangement of Laponite particles and lithium iodate nanocrystals due to their different (dielectric) properties. Indeed, the strong electrical contrast is associated with the sample topography. Secondly, since no coulombic interaction is detected in the $F_{\omega}$ signal, the negative charge of Laponite particles is screened, maybe by adsorbed water. Besides, no electrical contrast could be observed on non-altered surfaces shown in Fig. 4a.
6. Conclusion—Perspectives

The surface arrangement of Laponite particles and LiIO₃ nanocrystals in composite waveguides were studied by SFM techniques. Individual Laponite particles were imaged by IC-AFM as well as humidity-induced crystallisation of surface lithium iodate crystals for waveguides stored in ambient conditions. Electrostatic Force Microscopy with amplitude modulation was also used to obtain a “chemical contrast” of sample surface. The electrical contrast was attributed to sample topography and not to the properties of each constituent. Nevertheless, EFM can also be used to apply a strong local electric field. Being given that lithium iodate has a polar structure, our final aim is to orientate nucleus with a submicronic spatial resolution. The simultaneous inscription and control of nanocrystals orientation is a possible route to carry out periodic structures that can be used, in this case, for waveguided quasi phase matching (QPM).

References

5. Rockwood Specialties Inc., Product Data Sheet L/JS/2/01.