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Hybrid Sol–gel thin films for magneto-optical applications: Chemical, optical and tribological study

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Abstract

Sol–gel processes are promising strategies to prepare materials with synergetic or complementary behaviour between a polymer and an inorganic matrix interacting at the molecular scale. The conditions of soft chemistry allow the integration of photocurable organic compounds into an inorganic network, opening the way to the creation of new nanocomposite materials deposited on wide surfaces. The objective of the present study is to develop a process in order to prepare doped thin solid film for magneto-optical applications. The main steps of the process are the deposition (by hydrolysis condensation) and characterization of an organically modified silicon alkoxide containing zirconium alkoxide to modulate the refractive index of the film. After deposition, UV irradiation allows to develop an organic structure entangled in the inorganic network.

For various applications, tribological studies on these new materials cannot be bypassed since these future components may be submitted to various mechanical solicitations. The resulting thin films, exhibiting a high transparency with a modulable refractive index, have a great potential to be used for components in integrated optical devices. The friction and wear behavior of the films has been investigated depending on the deposition conditions, mainly the organic conversion ratio ranging between 6 and 98%. The organic conversion ratio corresponds to the range of organic network within the film. For the lowest organic conversion ratios, the films do not withstand the friction tests and exhibit poor wear resistance. For conversion ratios above 60%, friction coefficients in the 0.1 range have been recorded, with a significant wear resistance. The tribological behaviors of such inorganic-organic hybrid nanocomposite thin films tested in standard conditions are discussed in agreement with their structure and composition. The potentiality to reach both wear resistance and outstanding optical properties will be evaluated.

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Keywords: Sol–gel; Thin films; Tribology; Photopolymerization; Doping

1. Introduction

Sol–gel processes allow the production of a wide range of materials. The veritable explosion of interest in the Sol–gel route seems to result in large measure in the ability of obtaining thin solid films with a high degree of homogeneity for technological applications. Compared to thermal processed coatings such as chemical vapour deposition, Sol–gel processes offer the advantages of low energy consumption and the ability of coating wide surface of substrate [1]. The conditions of soft chemistry allow the integration of organic compounds into an inorganic network leading to hybrid inorganic-organic films. Hybrid Sol–gel coatings have recently gained interest because these nanocomposites combine the advantages of polymers (suppleness, light

weight) and those of mineral glass (hardness, refractive index, transparency, chemical stability.) [2]. As a result, these films are widely used for the development of micro-optical devices (microlenses and waveguides). Among these new optical elements, isolators and circulators for high speed communication use the non reciprocal functionality of magneto-optical material [3]. These applications need to dope the coatings with magnetic nanoparticles.

Recently, doped films such as maghemite nanoparticles embedded in a silica-titania matrix were investigated as promising candidates for magneto-optic application. Magneto-optical planar waveguides were made but their characteristics have to be improved. To use thin films as magneto-optical waveguides, it is necessary to optimize the TE-TM waveguide conversion R_M :

$$R_M = \frac{\theta_F^2}{\theta_F^2 + (k\Delta N)^2} \quad (1)$$

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θ_F (°/cm) is the specific Faraday rotation of the material constituting the waveguide.

This rotation is due to the magnetic dopant trapped in the gel. ΔN is the modal birefringence of the film linked to its residual stress. k is the wave number $k=2\pi/\lambda$ (λ the wavelength).

The maximum TE-TM conversion ratio we could expect with maghemite ($\gamma\text{-Fe}_2\text{O}_3$) doped silica/titania matrix is too low [4]. So the objectives of the present study are:

- to develop a new doping process in order to dope the layers with cobalt ferrite nanoparticles whose Faraday rotation θ_F is stronger than maghemite.
- to decrease the residual stress in the films in order to reduce the modal birefringence ΔN .
- to have a significant wear resistance for these coatings used as components submitted to various mechanical sollicitation.

2. Experimental procedure

2.1. Hybrid sol preparation

The hybrid sol is prepared from a combination of methacryloxytrimethoxysilane (MAPTMS), zirconium *n*-tetrapropoxide (ZPO) and methacrylic acid in molar ratio 10:1:1. In a first step, partial hydrolysis and polycondensation of methacryloxytrimethoxysilane is initiated with 0.75 equivalents of acidified water (0.01 M HCl) [5]:

$$\frac{n\text{H}_2\text{O}}{n\text{MAPTMS}} = 0.75 \quad (2)$$

In a second step, zirconium *n*-tetrapropoxide was complexed with methacrylic acid in order to avoid undesired precipitation of ZrO_2 [6]:

$$\frac{n\text{ZPO}}{n\text{MAA}} = 1 \quad (3)$$

The two solutions are mixed together and hydrolysis and condensation of the remaining silicon alkoxide functionalities and the zirconium *n*-propoxide are made by the addition of water:

$$\frac{n\text{H}_2\text{O}}{n\text{Alcoxyde}} = 1.5 \quad (4)$$

A photoinitiator in the form of 3 wt.% of 2,2-dimethoxy-1,2-diphenylethan-2-one (Irgacure 651 Ciba Geigy) is added to the sol.

2.2. Cobalt ferrite nanoparticles synthesis and characterizations

2.2.1. Cobalt ferrite nanoparticles synthesis

An aqueous mixture of cobalt nitrate ($\text{Co}(\text{NO}_3)_2$) and ferric chloride (FeCl_3) was made. The molar ratio between cobalt and iron is:

$$\frac{n\text{Co(II)}}{n\text{Fe(III)}} = 0.5 \quad (5)$$

The solution is abruptly added under vigorous stirring to a sodium hydroxide solution heated at boiling temperature. After stirring 5 min, a magnetic mixture is obtained [7].

The magnetic precipitate is then isolated from the solution by magnetic decantation. The mixture is then washed several times with a solution of nitric acid (0.01 M). The dispersion is then made by adding a right amount of nitric acid solution [8].

2.2.2. Nanoparticles characterizations

2.2.2.1. X-ray diffraction. The XRD spectra of the fine particles prepared show the same peaks as the CoFe_2O_4 XRD spectra of the library [9]. But, the experimental XRD spectrum is very close to the Fe_3O_4 XRD spectrum. A complementary analysis is required.

2.2.2.2. Determination of chemical element in the powders.

The concentrations of the metallic species were determined by inductive coupled plasma-atomic emission spectroscopy. After pyrolysis at 3000 °C the remaining oxygen is measured by infrared detection. Results are gathered in Table 1.

This analysis proves that synthesized nanoparticles are cobalt ferrite CoFe_2O_4 .

2.2.2.3. Faraday rotation measurement. Faraday rotation is analysed by ellipsometry. In our case, a linearly polarized light ($\lambda=822$ nm) is passed through the sample. The sample is submitted to a magnetic field whose direction is parallel to the light beam. Due to the Faraday effect, a rotation of the Faraday polarization is induced by this field in the material. At the output, the linear polarization makes an angle θ_F with the incident one. This angle is measured by an ellipsometer.

The specific Faraday rotation measured in our sample is strong. The saturated magnitude at high field is about 28°/cm. This value indicates that the volumic concentration of nanoparticles in the dispersion is about 2%.

2.3. Doping process

The introduction of a cobalt ferrite ferrofluid in the hybrid sol leads to precipitation. So we formulate jointly hybrid sol and cobalt ferrite doping. The insertion of aqueous cobalt ferrite dispersion is made by joint hydrolysis. This process ensures the stability of the dispersion of doping in the medium.

2.4. Coating procedure and thin films characterization

2.4.1. Coating procedure

Just before the coatings, the free-flowing sol is passed through a 0.2 μm filter. Cleaned glass slides and silicon wafer double polished are used as substrates. Just before the coating, the

Table 1
Chemical elements in the powders determined by ICP-AES and infrared detection

	Theoretical value	Sample 1	Sample 2	Sample 3
$n\text{Co}/n\text{Fe}$	0.5	0.4934	0.4838	0.4960
$n\text{Co}/n\text{O}$	0.25	0.2316	0.2135	0.2626

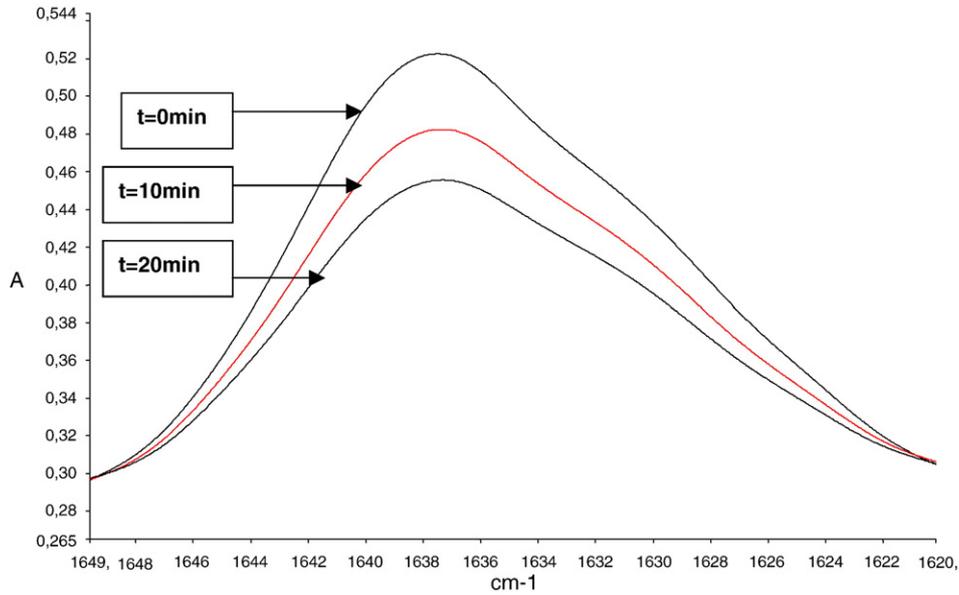


Fig. 1. Evolution of the area of the C=C vibration peak according to the irradiation time.

substrates are degreased with optical paper and ethyl alcohol. The hybrid thin films are elaborated by dip coating [10].

Trials were used to optimize the parameters and therefore:

- the withdrawal speed is 7 cm/min.
- the sol viscosity is 15 cP.
- the temperature is 21 °C and the relative humidity is 30%.

This coating procedure allows the production of doped hybrid thin films of optical quality.

2.5. Thin hybrid films curing

The UV irradiation induces the polymerization of the methacrylate chains of the silicon alkoxide and those of the methacrylic acid. The main curing parameters are:

- The power density of the irradiation measured at the sample surface ($4 \mu\text{W}/\text{mm}^2$ at $\lambda=254 \text{ nm}$; $6 \mu\text{W}/\text{mm}^2$ at $\lambda=365 \text{ nm}$).

- The treatment duration.
- The use of a thermally assisted UV curing.

2.6. Evaluation of the organic conversion ratio by infrared spectroscopy

The photoinduced organic polymerization results in decrease in intensity of the C=C band at 1637 cm^{-1} .

The residual monomer concentration is monitored by the calculation of the area of the 1637 cm^{-1} metacrylate band. The organic conversion ratio is defined as the ratio of the residual monomer function to its zero value [11]:

$$\%C = 100 * \left(\frac{A(t=0) - A(t)}{A(t=0)} \right) = 100 * \left(1 - \frac{A(t)}{A(t=0)} \right) \quad (6)$$

where A_t et $A_{t=0}$ are the areas of the 1637 cm^{-1} peak at times t and $t=0$ respectively.

2.7. Measurement of the friction coefficient of the films by means of tribological analysis

The tribological behaviour of the hybrid films has been studied at room temperature using a reciprocating pin-on-flat

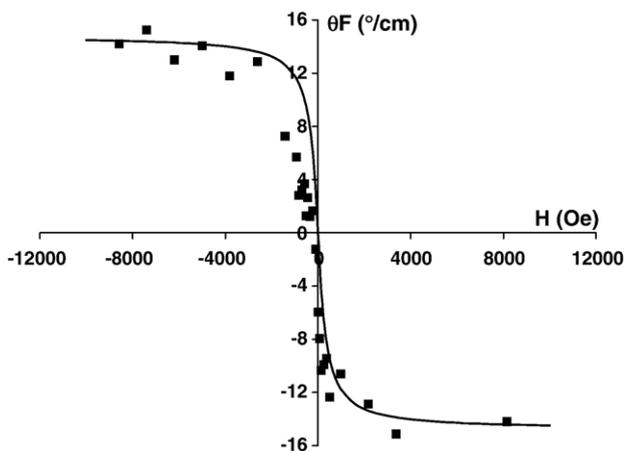


Fig. 2. Faraday rotation of a $2.9 \mu\text{m}$ thick sample measured at $\lambda=820 \text{ nm}$. H is the longitudinal applied magnetic field.

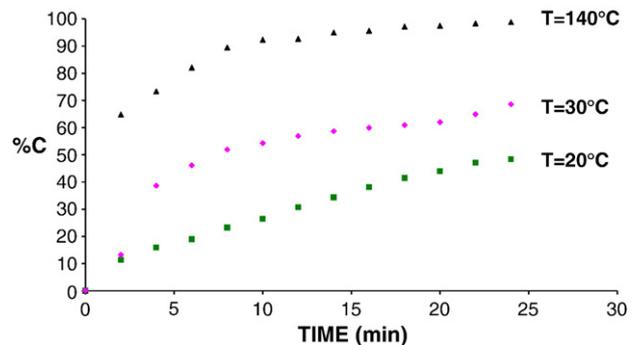


Fig. 3. Influence of temperature curing on photopolymerisation kinetics.

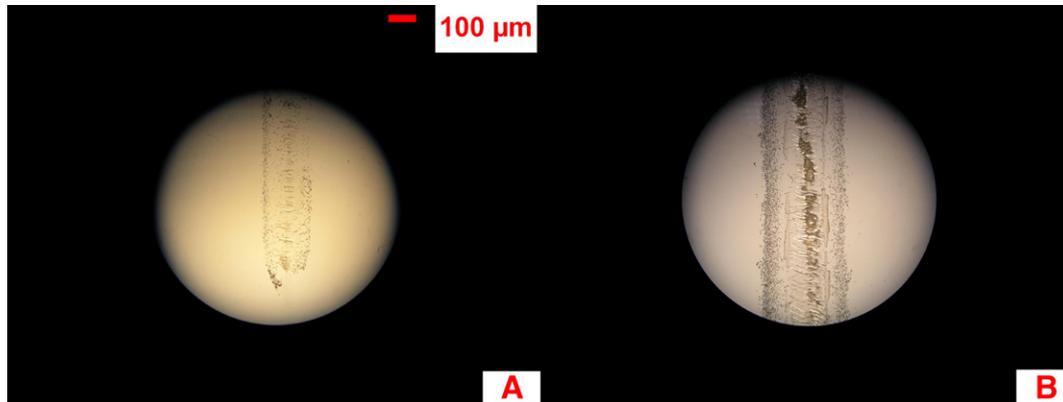


Fig. 4. Optical micrograph of the wear track related to the hybrid film deposited on silicon with a conversion ratio of 86% after A) 100 cycles B) 1000 cycles (normal load 1 N).

configuration in ambient air (28–30% relative humidity). The evolution of the friction coefficient versus the organic conversion ratio was recorded using AISI52100 steel round balls (6.00 mm diameter) sized for normal applied loads between 0.5 and 3 N. The sliding speed was 1 mm/s over a 1.5 mm long wear track. The wear resistance was estimated for different organic conversion ratio (see Fig. 1).

3. Results and discussion

3.1. Magneto-optical characterization

Ellipsometric analysis of the light state of polarization evidenced the realization of magneto-optical planar waveguide on glass substrate. Fig. 2 reports the specific Faraday rotation of a doped hybrid thin film. It has been measured on a 2.9 μm thick cobalt ferrite doped sample deposited on a glass substrate. This film was UV treated using power of 1200 mW/cm² during 15 min. The refractive index of this film is 1.52 (measured using M-lines spectroscopy at λ=633 nm).

The obtained curve has a nonreciprocal behaviour typical of the Faraday effect. The saturated magnitude at high field is about 15°/cm. This value indicates that the volume fraction of nanoparticles in the film is about 0.15%.

Compared this result with the previous work of Royer and al [4] the hybrid Sol–gel films doped by cobalt ferrite are very interesting to realize a magneto-optical waveguide. To improve the properties of these waveguides, the nanoparticles volume fraction has to be increased in the material.

3.2. Study of the effect of the treatment's parameters on thin films properties

3.2.1. Modulation of the photopolymerisation kinetics

After deposition, UV irradiation allows to develop an organic structure entangled in the inorganic network by a well known mechanism of propagation and termination. The organic conversion ratio corresponds to the range of organic network within the film. It was verified by ¹³C NMR experiments that consumption of C=C leads to new C–C bonds [12].

The conversion ratio is studied versus the irradiation time and also versus thermally assisted UV curing process. Fig. 3 shows the kinetics of the conversion ratio for compositions 10:1:1. when samples were irradiated with a power density of 4 μW/mm² at λ=254 nm. The different temperatures were 20, 30 and 140 °C.

The curves' shapes are typical for an acrylate system. The induction period is short and the polymerisation rate increases

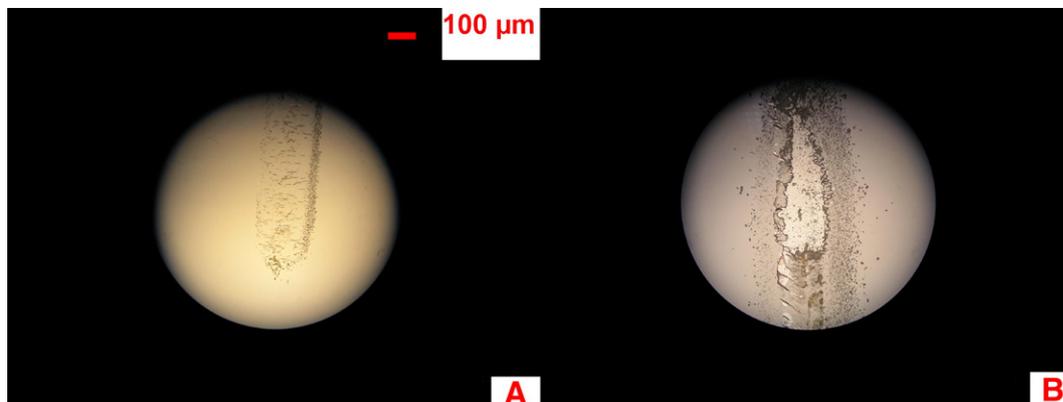


Fig. 5. Optical micrograph of the wear track related to the hybrid film deposited on silicon with a conversion ratio of 86% after A) 100 cycles B) 1000 cycles (normal load 3 N).

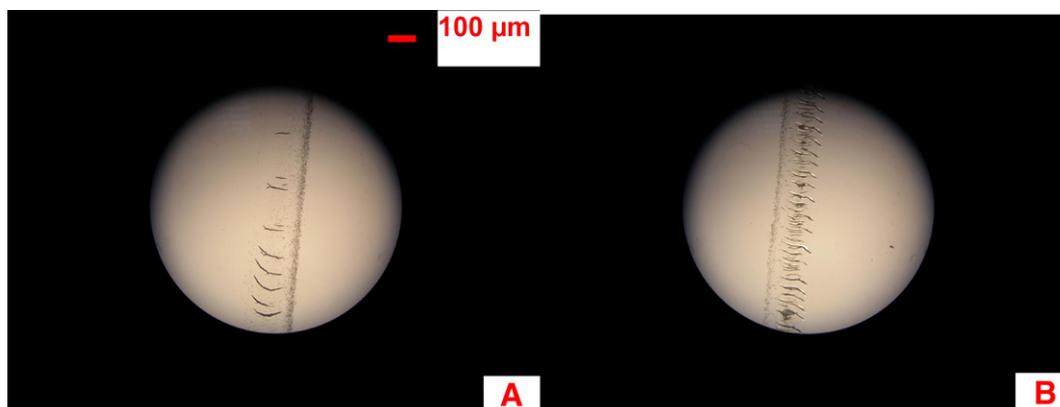


Fig. 6. Optical micrograph of the wear track related to the hybrid film deposited on silicon with a conversion ratio of 60% A) normal load 1 N B) normal load 3 N (100 cycles).

quickly because of the high dissociation efficiency of the photoinitiator. A plateau of the polymerisation ratio is reached when the mobility of polymerisable moieties is too low.

The effect of curing temperature on photopolymerisation kinetics is shown clearly: the polymerisation kinetics is faster at higher curing temperature. For an irradiation time of 10 min, the conversion ratio reaches 26% at 20 °C, 50% at 30 °C and 90% at 140 °C. The modulation of photopolymerisation kinetics is used to decrease the modal birefringence ΔN . Organic network adds flexibility to the film. So, it allows decreasing mechanical stress [13].

3.2.2. Tribological studies of hybrid thin films

The objective is to identify the effect of the conversion ratio on the friction and wear behaviour of the hybrid films deposited on silicon. Fig. 4 shows the wear tracks of the silicon plane coated with a hybrid film with a conversion ratio of 86% after 100 cycles and 1000 cycles performed with a normal load of 1 N.

The film withstands the sliding test, even if some cracks are visible in the centre of the tracks. These tracks are probably due to the brittle character of the silicon substrate, since a stable friction coefficient in the 0.1 range representative of the lubricative property of the film is observed during the friction test.

When the normal load increases, the wear tracks are deeper, as seen in Fig. 5 showing the tracks performed with a normal load of 3 N. With a conversion ratio of 60%, the wear behaviour is very similar to the previous one. Fig. 6 shows the wear tracks after 100 cycles for a coating with a conversion ratio of 60%. The tracks show that the film withstands the friction test for a normal load of 1 N and also 3 N.

For these samples with a conversion ratio >60%, we found a load depend friction coefficient: when the load increases, the friction coefficient decreases. Results are reported in Table 2.

This load dependence is explained by the Hertzian contact model [14]. This model is based on the pressure dependence of the shear strength. Thus, the friction coefficient under Hertzian contact is load dependent.

Fig. 7 shows the wear track related to the hybrid film with a conversion ratio of 6%. Such a low conversion ratio induces a

rapid destruction of the film during the tribological test, as observed in this figure.

The organic network is too weak to withstand the shearing process induced by the friction test. The same behaviour is observed for a layer with a conversion ratio of 17% (not shown).

The influence of the conversion ratio on the tribological behaviour can be resumed as follow:

- For the lowest organic conversion ratios (6 and 17%), the films do not withstand the friction tests and exhibit poor wear resistance.
- For conversion ratios above 60%, friction coefficients in the 0.1 range have been recorded, with a significant wear resistance.

The tribological behaviors versus the various conversion ratios show that the highest conversion ratios allow to reach a significant higher wear resistance in severe sliding conditions, compared to lower conversion ratios. In the present set of films, a conversion ratio of at least 60% ensures a friction behaviour and a wear resistance corresponding to usual solid lubricant films. From the optical micrographs (Figs. 4–7) and the systematic observation of the steel pin uncoated counterface, the friction mechanism of the wear resistant films does correspond to an interfilm sliding mechanism, with the initial formation of a tribofilm from the first sliding cycles. Indeed interfilm sliding is one of the most usual tribological mechanism in solid lubrication [15]. The steady-state friction coefficient recorded in the 0.1 range shows that the wear behaviour of the hybrid layers is typical of films whose composition is located between hard mineral coatings and soft organic films [16]. Such basic tribological investigations on these new materials cannot be

Table 2
Average friction coefficients for different organic conversion ratios

Conversion ratio (%)	Average friction coefficient after 100 cycles with a normal load of 1 N	Average friction coefficient after 100 cycles with a normal load of 3 N
60	0.19	0.02
86	0.18	0.10
97	0.18	0.13

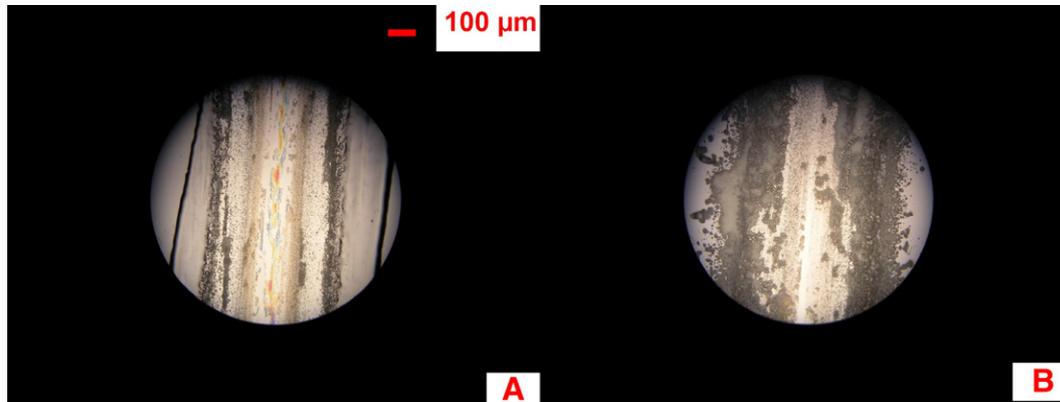


Fig. 7. Optical micrograph of the wear track related to the hybrid film deposited on silicon with a conversion ratio of 6% after 100 cycles A) normal load 1 N B) normal load 3 N.

bypassed since the future components coated by such films may be submitted to various mechanical solicitations. The coatings with a conversion ratio <60% are unable to withstand the friction test and so these films can't be used for magneto-optical waveguides applications.

4. Conclusion

Transparent, cobalt ferrite doped hybrid thin films have been prepared. Due to the choice of joint hydrolysis of the sol and the doping, it is possible to introduce cobalt ferrite in the sol without precipitation. These doped films evidenced the realization of magneto-optical planar waveguide on glass substrate. The use of a hybrid organo-metallic Sol–gel matrix with the appropriate conversion ratio can reduce the intrinsic birefringence. It was observed that the modulation of the photopolymerisation kinetics can be used to decrease the mechanical stress in the coatings. The weaker conversion ratios are the most efficient for the stress decrease. However, conversion ratio <60% induce materials with a wear behaviour incompatible with their use as future optical integrated devices. Low conversion ratios are restrictive if using the material for optical application.

The thin coatings' characteristics have to be improved to use such doped hybrid films as optical compounds.

Doping the material with more cobalt ferrite nanoparticles is essential to ensure a strong Faraday rotation in the solid gel used as magneto-optical waveguide. The choice of an appropriate organic conversion ratio is necessary both to decrease the mechanical stress in the layer and to ensure minimal wear behaviour compatible with their use.

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