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# The effect of the viscosity in the precursor solution on the structure of sol-gel derived silica films containing cobalt

H. TOTOTZINTLE-HUITLE, A. RAMOS-MENDOZA, A. MENDOZA-GALVÁN, J. GONZÁLEZ-HERNÁNDEZ
*Centro de Investigación y de Estudios Avanzados del IPN, Unidad Querétaro,*
*Apartado Postal 1-798, 76001, Querétaro, Qro., México*
*E-mail: amendoza@ciateq.mex*

B. S. CHAO
*Energy Conversion Devices, Inc., 1675 W. Maple Rd., Troy, MI, 48084, USA*

Silica coatings containing cobalt have been prepared from sol-gel precursor solutions having a viscosity in the range of 3 to 40 cP. The different values of viscosity were achieved by aging the solutions with various amount of solvent (ethanol). The structure of these samples was analyzed using x-ray diffraction, Raman scattering, infrared absorption and Auger depth profiles. These measurements show that, upon heat treatments in air at 500°C, the cobalt oxidizes to form small oxide particles. However, when the coatings are prepared from precursor solutions with viscosity lower than about 9 cP, the cobalt migrates to the outer surface of the coating were it is oxidized to form the particles. On the other hand, if the coatings are prepared from solutions with a higher viscosity, the oxide particles are formed in the bulk of the coating. The infrared and Raman spectra indicate that the structure of this later set samples is more ordered with fewer amount of voids.

## 1. Introduction

Silica films are widely used for several applications. Different techniques have been implemented to prepare these materials and their structure and properties depend not only on the preparation technique but also on the specific deposition parameters. For certain applications the sol-gel method has proved to be useful to produced good quality $SiO_2$ coatings, fibers and powdered material [1–3].

Numerous reports have indicated that the physicochemical structure of dissected gels is a result of a complex sequence of hydrolyzation, gelation, and drying conditions employed during processing [4–8]. The structure of sol-gel derived $SiO_2$ coatings is also dependent on the incorporation of other spices (atomic, molecular and/or particles) and on the treatments applied during and/or after coating processing. In fact, several authors have shown that the microstructure of a bulk $SiO_2$ glass is different than that of a thin coating due to the faster drying process of the later [9, 10]. This difference in the microstructure may be rationalized in the following terms: in bulk glasses, the gelation occurs slowly and in the presence of the organic solvent, generally an alcohol. Thus, the polymerizing oxide phase tends to form small particles. On the other hand, for coatings, the polymerization takes place simultaneously to the evaporation of the solvent and there will be an enhanced polycondensation, forming a more closed structure.

J. R. Martínez *et al.*, have shown that in silica gels prepared from solutions based on the tetraethylorthosilicate (TEOS), the variation of the $H_2O$/TEOS ratio in the precursor solution, in the range of 3 to 12, produces $SiO_2$ samples with different structures [4]. They show that low $H_2O$/TEOS ratios, produce samples with a polymer structure, whereas the structure of samples prepared from solutions with larger ratios have a three dimensional structure. Recently it has been shown that some metals such as Ag and Cu modify the amorphous structure of sol-gel $SiO_2$ samples in a way that crystallization of the silica occurs at temperatures lower than 500°C [11]. Several reports have appeared relating structural changes in silica coatings produced with treatments after deposition. Thermal treatments, at temperatures above 800°C densify silica films [12–14]. Similar densification effects have been found in these types of coatings when they are subjected to irradiation with ultraviolet photons [15, 16] or with energetic particles [17].

In sol-gel prepared $SiO_2$ glasses doped with cobalt, most of previous studies have been focused on the investigation of the optical properties produced by the $Co^{2+}$ ions [18, 19]. In those studies, it was found that exceeding certain amount of cobalt, cobalt oxide particles are

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formed upon thermal treatment under an oxidizing atmosphere. However, it has been recently reported that in $SiO_2$ coatings with cobalt, prepared under specific conditions, the cobalt migrates to the coating free surface to form a rich $Co_3O_4$ layer, which modifies largely the optical properties of the coatings, [20, 21]. The purpose of the present work, is to analyze the structure of silica sol-gel coatings containing cobalt. The cobalt concentration for sample preparation was chosen to allow the formation of cobalt oxide. It is concluded that the structure of the coating depends on the aging time ($t_a$), or equivalently on the viscosity ($\eta$) of the precursor solutions. Coatings prepared from solutions with a viscosity lower than about 9 cP show a more opened structure than those prepared from solutions with larger viscosity. Depending on the structure, the cobalt oxide is formed either at the free surface of the coating or inside the bulk. The results are deduced from x-ray diffraction, Auger atomic depth profiles, and infrared measurements.

## 2. Experimental methods

The coatings were prepared by the sol-gel method on infrared transparent silicon wafer substrates. The sol-gel precursor solutions were obtained mixing TEOS, ethanol and water at the following molar ratios: ethanol to TEOS, 4 to 1 and water to TEOS, 11.7 to 1. Cobalt nitrate was used as the source of cobalt. According to the amount of cobalt nitrate added to the precursor solution, the coatings have a nominal Si to Co atomic ratio of 1.8. This value assumes that all the silicon is converted into silica, and that all the cobalt is dissolved into the precursor solution. The coatings were deposited using the dip coating method, at a withdrawal speed of 10 cm/min, with this parameters the thickness of the coatings was of about 500 nm. All coatings were dried at a temperature of 180°C for 10 min under air conditions. Subsequent thermal treatments were performed in air at temperatures of 300 and 500°C for 15 min.

The x-ray diffraction (XRD) measurements were obtained using a Rigaku diffractometer equipped with copper radiation. Auger electron spectroscopy was performed to obtain the atomic depth profile. The infrared (IR) and Raman measurements were carried out using a Nicolet model 205 spectrophotometer and a Dilor micro Raman system, respectively. A He-Ne laser with a maximum power of 20 mW, focussed to few micrometers, was used for excitation in the Raman measurements. The viscosity ($\eta$) of the solutions was measured using a Brookfield DV-I viscometer. The $\eta$ value was measured as a function of the aging time ($t_a$) of the precursor solutions, until $\eta$ was above 40 cP. At this viscosity the coating did not show good characteristics.

## 3. Experimental results

Fig. 1 shows the viscosity curves versus $t_a$ for three precursor solutions with different compositions. The three viscosity curves were obtained from solutions that were prepared from the same starting solution with an ethanol: TEOS and $H_2O$:TEOS ratios of 4 : 1 and 11.7 : 1, respectively. This starting solution, with a total volume of 180 ml, was separated in three equal parts. One of these parts was kept with the same composition, this was named solution 1 (curve 1, Fig. 1). To each one of the other two parts 30 ml of additional ethanol were added 2 hours after the starting solution was prepared. Curve 2 corresponds to one of these two solutions (solution 2). Curve 3 corresponds to the third starting solution (solution 3) with another 30 ml of ethanol added 72 hours after the starting solution was prepared. Thus, this third solution had 60 ml more ethanol than the original starting solution. In Fig. 1 the black symbols represent the measured data points, the continuos curves were drawn to guide the eye. As can be observed, the viscosity for the three solutions has similar behavior, that is, it first increases slowly and for longer aging times it increases rapidly. The time at which the viscosity of the solution increases abruptly can be defined as the gelation time. This time is about 144, 340 and 455 hours for solution 1, 2 and 3, respectively. The addition of larger amount of solvent (ethanol) clearly increases the gelation time of the solution. It should be notice that the three solutions have a viscosity of about 9 cP when the gelation time reached, this critical viscosity will be denoted hereafter as $\eta_c$.

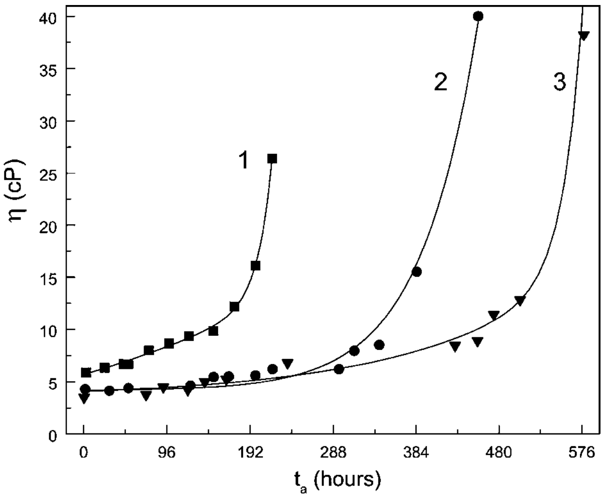

*Figure 1* Viscosity versus aging time for three sol-gel precursor solutions. The data denoted with the dots and triangles corresponds to solutions to which additional ethanol was added.

Fig. 2 shows the XRD patterns for two coatings prepared from solution 3 when its viscosity was 5 (top) and 12 (bottom) cP. Both coatings were heated in air at 500°C for 15 minutes. Weak diffraction lines appear in both patterns that indicate the formation of $Co_3O_4$ with the cubic spinel structure. The vertical lines indicate the position and relative intensity of a commercial $Co_3O_4$ powdered sample with the same cubic structure. Notice that the samples prepared from the solution with lower viscosity show less intense diffraction lines. From the main diffraction line the estimated size for cobalt oxide particles is about 20 nm. Thermal treatments at 300°C in similar samples show x-ray patterns with the presence of the $Co_3O_4$ phase but with less intensity. Similar results were observed in coatings prepared from solutions 1 and 2.

In Fig. 3 are shown the Raman scattering spectra for three samples. Spectra (b) and (c) correspond to coatings prepared from the solution 3 when its viscosity

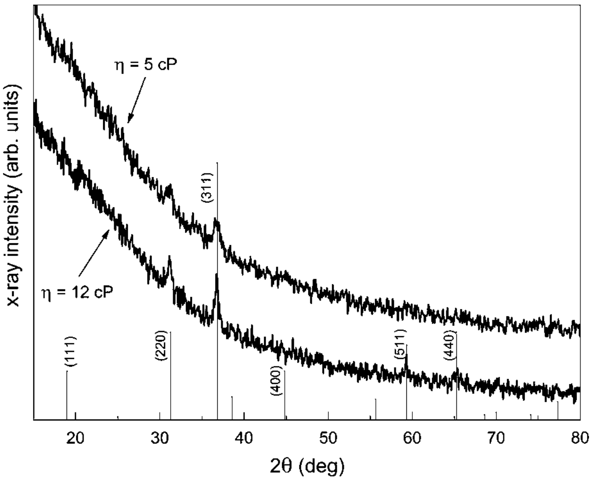

*Figure 2* X-ray diffraction patterns from two coatings obtained at the viscosity values indicated and heat-treated at 500°C.

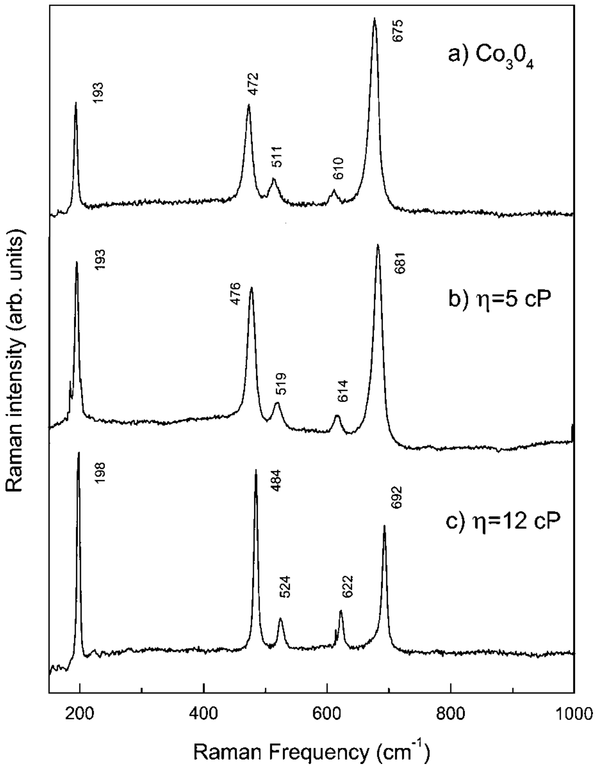

*Figure 3* Raman spectra for two $SiO_2$ coatings with cobalt annealed at 500°C, and prepared from solutions with a viscosity of 5 (b) and 12 (c) cP. Spectrum (a) was obtained from calcinated cobalt nitrate at 500°C.

was 5 (b) and 12 cP (c). These two samples were heat treated in air at 500°C for 15 min. The spectrum (a) was obtained by calcinating the cobalt nitrate (used as the source of cobalt) at 500°C in air for 10 min. In this spectrum, the four bands in the range of 470–700 $cm^{-1}$ are consistent with those reported in the literature for $Co_3O_4$ films [22]. These results not only corroborate the XRD results but also show that the Raman technique is more sensitive in the detection of the cobalt oxide. It is clear that the Raman lines in the spectrum (c) are narrower and shifted to higher frequencies than those in spectra (a) and (b), this indicates that the cobalt oxide particles in the former case (c) are of a larger size [23, 24]. This result agrees with the XRD data which shows less intense diffraction lines for samples prepared from solutions with lower viscosity. Similar results were obtained in coatings prepared from solutions 1 and 2.

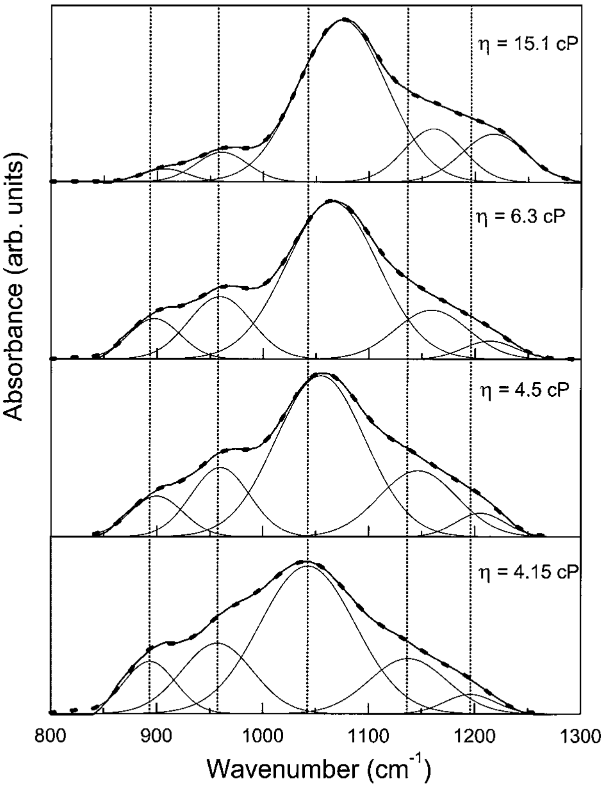

*Figure 4* Infrared absorption spectra for $SiO_2$ coatings with cobalt prepared from solutions with the indicated value of viscosity.

Typical IR data, in the range of 800 to 1300 $cm^{-1}$, are shown in Fig. 4 for coatings prepared from solution 2 when its viscosity was 4.15, 4.5, 6.3 and 15.1 cP. After the samples were made, all of them were heated in air at 500°C for 15 min. The measured spectra (continuous heavy curves) have been decomposed in five absorption bands (continuous light curves), using gaussian expressions. The sum of these five bands is represented by the dots. The two absorption bands in the range of 890–960 $cm^{-1}$ have been previously associated with vibrations of silanol (Si—OH) groups [18], with two different local environments. Notice that the position of these bands does not depend on the viscosity of the precursor solution and that their relative intensity decreases with the increase of the precursor solution viscosity. The band in the range of 1040–1075 $cm^{-1}$ is associated with the asymmetrical Si—O bond stretching vibrations [4, 25, 26]. Sub-bands in the range of 1130–1220 $cm^{-1}$ have been previously reported at positions closed to those in Fig. 4 [27, 28]. In general it has been observed that the relative amplitude of these sub-bands increases with the increase in the structural disorder in the $SiO_2$ amorphous network [4, 29]. From the data in Fig. 4, it can be observed that the position of the main stretching band and that of the sub-bands depends on the viscosity of the precursor solution. The main stretching band is at 1042 $cm^{-1}$ in coatings prepared from solutions with $\eta = 4.15$ cP and it gradually shifts to larger wavenumbers with the increase in $\eta$, having a position of 1074 $cm^{-1}$ when $\eta = 15.1$ cP. The sub-bands at the

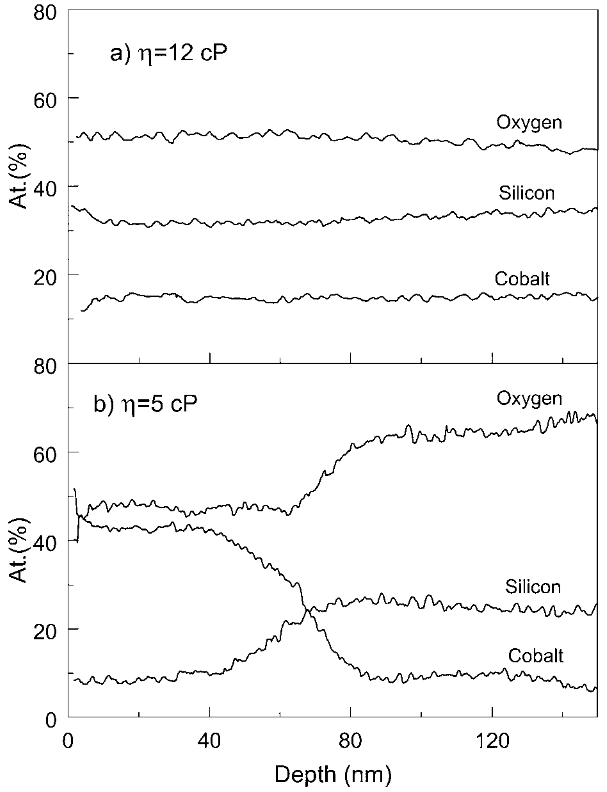

*Figure 5* Typical oxygen, silicon and cobalt atomic Auger profiles for coatings prepared from solutions with a viscosity above (a) and below (b) 9 cP.

right hand side of the main stretching band also show similar shifts.

Fig. 5 shows typical atomic Auger depth profiles for oxygen, silicon and cobalt for two samples prepared from solution 3 at two different values of $\eta$. These coatings were annealed at 500°C for 15 min. The profiles in Fig. 5a correspond to samples prepared from the solution with $\eta = 12$ cP and those in Fig. 5b to coatings with $\eta = 5$ cP. Samples prepared from solutions with $\eta$ higher than 9 cP have Auger profiles similar to those shown in Fig. 5a, whereas coatings prepared from solutions with $\eta$ lower than 9 cP show Auger depth profiles similar to those in Fig. 5b. The Auger results show that coatings prepared from solutions with $\eta \geq \eta_c$ have a constant oxygen, silicon and cobalt atomic profile (Fig. 5a), whereas coatings prepared from solutions which have $\eta < \eta_c$ show atomic profiles which depend on depth (Fig. 5b). In this latter case, most of the cobalt is at the free surface of the coating in a layer of about 60 nm; this layer has less silicon and less oxygen than the bulk of the coating.

## 4. Discussion of results

As shown in Fig. 1, the viscosity of the precursor solution continuously increases with the aging time [1]. However, during the gelation-condensation process two different regimes are clearly observed. These two regimes can be characterized by the rate of change in the viscosity of the solution. The first regime corresponds to the initial steps of hydrolyzation/gelation of the solution, and it is characterized by a low rate of change in $\eta$. This occurs for $\eta \leq \eta_c$. The second regime corresponds to the gelation/condensation process, characterized by a rate of change in $\eta$ fifty times larger. This is the case for $\eta \geq \eta_c$. As was mentioned before, $\eta_c$ is of about 9 cP and does not depend on the composition nor on the history of the precursor solution. In molecular terms, the first regime is probably related with the hydrolyzation and the formation of long chain molecules cross-linked together to create branched clusters, which could or could not interpenetrate prior to gelation. The second regime is related with gelation, which occurs when the clusters link together to form a tangled network which extends through the liquid.

The XRD and Raman results in Figs 2 and 3, respectively, indicate that the heat treatments in air at 500°C produce cobalt oxide particles, regardless of the $\eta$ value. However, according to the Auger profiles, when the precursor solution employed to prepare the coatings has a viscosity less than $\eta_c$, the cobalt oxide particles are formed in the surface of the coating. If the coatings are prepared from solutions with a viscosity higher than $\eta_c$, the cobalt oxide particles are formed in the bulk of the coating, with a fairly homogeneous spatial distribution, showing an atomic profile independent of depth. These results indicate that in the former case, most of the cobalt has migrated to the exterior surface of the coating, where it is oxidized by the atmospheric oxygen.

In previous publications we have analyzed the effect of cobalt concentration and annealing conditions on the optical properties of $SiO_2$ coatings containing cobalt, deposited on glass substrates from precursor solutions with viscosities lower than $\eta_c$ [20, 21]. It was found that for Si to Co atomic ratios of 3.1 and 7.1, cobalt remains as $Co^{2+}$ ions in four-fold coordinated sites for annealing temperatures as high as 500°C [20]. Also, in that work we found that in coatings with Si to Co atomic ratios of 1.3 and 1.8 annealed at 300°C, there is some evidence that the $Co^{2+}$ ions are at both four and six-fold coordination sites. Increasing the annealing temperature the formation of a rich $Co_3O_4$ top layer is promoted, which changes drastically the optical properties of the coatings [20]. The formation of the rich $Co_3O_4$ top layer was studied in more detail as a function of annealing temperature and annealing time for a Si to Co atomic ratio of 1.3, where a parabolic behavior of the layer thickness with annealing time was found. The latter suggest a diffusion-controlled process [21].

From the above paragraphs two cases can be distinguished. In one, cobalt diffuses to the external surface of the coating to form the $Co_3O_4$ top layer. In the other, the atmospheric oxygen diffuses into the coating, which is accompanied by diffusion of cobalt inside the coating to nucleate the cobalt oxide particles. These arguments indicate that the mobility of cobalt in samples prepared from solutions with $\eta \leq \eta_c$ is faster than the corresponding to samples prepared from solutions with $\eta \geq \eta_c$. Considering cobalt oxide particles with a size of about 20 nm, uniformly distributed in the volume of the coating ($\eta \geq \eta_c$), it can be estimated that the average diffusion length for cobalt is less than 20 nm. In the other case ($\eta \geq \eta_c$) this diffusion length is at least of the order of the coating thickness (500 nm). These results

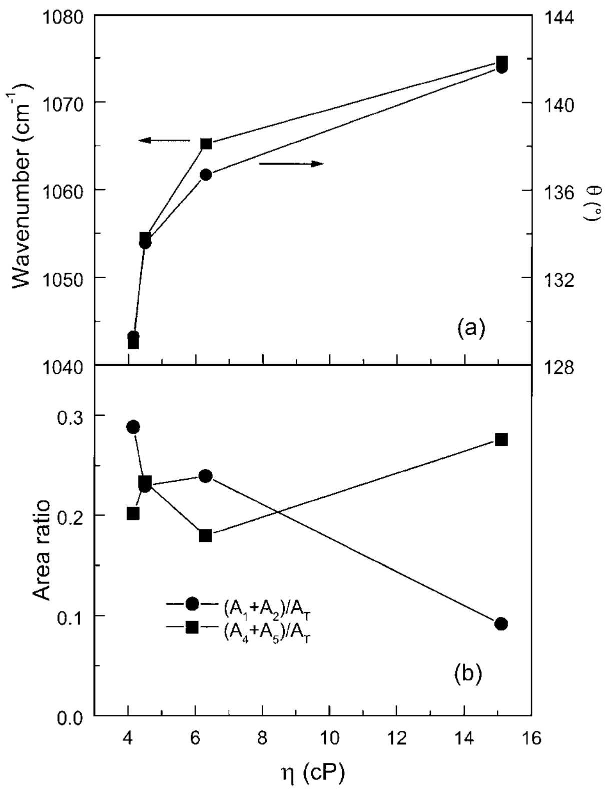

*Figure 6* (a) Change in the position of the Si—O stretching band and average Si—O—Si bridging bond angle. (b) Area ratios for the Si—OH groups (circles) and for the high frequency stretching sub-bands (squares).

indicate that the samples prepared from solutions with lower viscosity have a more opened structure.

The analysis of infrared data in Fig. 4 shows trends that support the latter conclusion. As was mentioned above, there is an up-shift in the position of the stretching band, which indicates densification of the silica matrix and an increase in its structural ordering, in a manner similar to thermal treatments [14, 30, 31]. In Fig. 6a is shown the wavenumber position (solid squares) of the gaussian curve corresponding to the asymmetrical Si—O bond stretching vibration as a function of viscosity. With these values it is possible to calculate the average Si—O—Si bridging bond angle ($\theta$), which according with the central force model [32] is given by:

$$\omega^2 = \frac{\alpha}{m_{\mathrm{O}}}(1-\cos\theta) + \frac{4\alpha}{3m_{\mathrm{Si}}}, \tag{1}$$

where $\omega$ is the angular frequency, $\alpha$ is the Si—O bond-stretching constant, and $m_{\mathrm{O}}$ and $m_{\mathrm{Si}}$ are the masses of the oxygen and silicon, respectively. The value of $\alpha$ was calculated using Equation 1, knowing that for $\omega = 1080\ \mathrm{cm}^{-1}$ corresponds a $\theta = 144°$. The $\theta$ values (solid circles) in Fig. 6a were obtained using the calculated $\alpha$ value.

In Fig. 6b are shown the calculated area ratios, $(A_1 + A_2)/A_{\mathrm{T}}$ and $(A_4 + A_5)/A_{\mathrm{T}}$, for the two bands associated with the Si—OH groups, and for the two sub-bands coupled to the main stretching band, respectively. $A_{\mathrm{T}}$ is the total area in the spectra of Fig. 4.

The data in Fig. 6 show that the concentration of OH groups decreases and the average bridging bond angle increases with the increase in $\eta$. Less OH groups indicates less internal surface area or less voids [1, 3, 4], which diminishes the strain in the network resulting in more ordered structure.

## 5. Conclusions

Thin $\mathrm{SiO_2}$ coating, containing cobalt have been prepared from sol-gel precursor solutions having a viscosity in the range of 3 to 40 cP. It is observed that in coatings prepared from solutions with a viscosity lower than about 9 cP, heat treatments in air at 500°C produce the migration of most of the cobalt to the outer surface of the coating to form a cobalt oxide layer of about 60 nm. In the other hand, in coating prepared form solutions with higher viscosity and heat treated at the same temperature, the oxide particles are formed in the volume of the coating. The analysis of the infrared absorption spectra for these samples indicates that there are fewer voids and a more ordered $\mathrm{SiO_2}$ structure in coatings prepared from solutions with higher viscosity. Samples prepared from solutions with lower viscosity have more voids, through which cobalt migrates easier.

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