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# **First results of humidity sensors based on CeO<sub>2</sub> thick film deposited by a new deposition technique from a suspension of nanoparticles**

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## Abstract

In this paper, we show the possibility to deposit a CeO<sub>2</sub> thick film on (111) silicon substrate from a suspension of CeO<sub>2</sub> nanoparticles by a new process of thick layer deposition in order to realize a humidity sensor. This new technique is derived from the spin-coating technology. The suspension is based on ultra-fine grinding of CeO<sub>2</sub> firstly in a stirred media mill coupled then in a sonication cell. Suspension viscosity has been adjusted with carbopol polymer and its rheological properties have been analyzed in order to cover completely the silicon substrate by the CeO<sub>2</sub> layer. Then, the impact of a conventional annealing on the crystallinity of the CeO<sub>2</sub> film has also been investigated by Raman spectroscopy and by scanning electron microscopy. Finally, gold interdigitated electrodes have been screen printed on the thick film surface in order to realize a sensor and first promising results on the humidity sensitivity have been highlighted.

## 1. Introduction

In the last decade, humidity sensors have gained increasing interest because monitoring and controlling humidity is not only useful in many industrial processes such as in automotive, agriculture, alimentary, pharmaceutical, and semiconductors industries but also in domestic electrical appliances [1-3]. Humidity sensors suitable in these practical applications require a high and linear response, a fast response, a recovery behavior, a small hysteresis, a wide humidity detection range, a long-term stability, and a low cost [4]. The performances of humidity sensors are mainly related to the properties of the sensing materials. So, a wide variety of materials for humidity sensors have been studied such as ceramic [1, 3, 5], organic polymer [6, 7], metal oxides [8-11], porous silicon [12], nano-porous silicon arrays [13], carbon nanotubes [14], cerium oxide nanowires, cerium oxide nanoparticles [4, 15-18] and multi-walled carbon nanotube thin films [19]. Many papers have reported on studies concerning the humidity sensitivity of metal oxide using  $\text{Al}_2\text{O}_3$  [20-22],  $\text{TiO}_2$  [10, 23-25],  $\text{SnO}_2$  [9, 26, 27],  $\text{TiO}_2\text{-SnO}_2$  [8],  $\text{ZnO}$  [9, 11, 28] and  $\text{ZrO}_2$  [29, 30] as sensing material. In fact, metal oxide materials have been mainly investigated due to their chemical and physical stability, high mechanical strength and wide operating temperature range [17, 31]. Several recent papers have highlighted the interest of nanostructured metal oxide material for the realization of humidity sensors because of their high surface to volume ratio and eventual changes in physical and chemical properties resulting from the quantum size effect [31]. Moreover, nanometer materials are characterized by small grain size and large specific surface area leading to more surface-active sites and a better sensitivity [29]. For these reasons, a focus on nanometer materials as  $\text{Al}_2\text{O}_3$  nanotubes [22], nanocrystalline  $\text{TiO}_2$  films [10],  $\text{TiO}_2$  nanotubes [25],  $\text{SnO}_2$  particles [26],  $\text{SnO}_2$  nanowires [27],  $\text{ZnO}$  nanowires [32],  $\text{ZnO}$

materials [11], ZnO nanorods [28], ZrO<sub>2</sub> nanorods [30], CeO<sub>2</sub> nanowires [15, 16], and CeO<sub>2</sub> nanoparticles [17, 18] has been done. For the latter material, Thakur et al. [4, 17] have recently reported that the sensors exhibit a high and linear response within the entire relative humidity (RH) ranging from 11 up to 97% at an operating frequency of 60 Hz. At the same time, the impedance of the sensor changes from  $3.91 \times 10^8$  down to  $3.58 \times 10^5 \Omega$  when RH increases from 11 up to 97%. Then the response and recovery times are approximately 3 and 16 s, respectively. A high sensitivity and a good linearity have also been highlighted by Xie et al. for sensor based on CeO<sub>2</sub> nanoparticles [18]. Effectively, they have shown that the complex impedance modulus decreases from  $3.8 \times 10^7$  down to  $4.3 \times 10^3 \Omega$  when the relative humidity rises from 11 up to 98% and that the response and recovery times were 10 and 3 s, respectively. Fast humidity sensors based on CeO<sub>2</sub> nanowires have also been done [15, 16] and response and recovery times of 3 s have been obtained. In the literature, CeO<sub>2</sub> materials can be made using different well known growth methods notably in the field of microelectronics, as pulsed laser deposition, sputtering, organic chemical vapor deposition, molecular beam epitaxy [33-42]....

However, it also possible to use other techniques such as spray pyrolysis [43], sol-gel process [44], hydrothermal method [15], rapid microwave-assisted method [17], solvothermal method [18], and sonochemical [45] methods. Once again, it is important to point out that low cost technologies must be involved to realize humidity sensors [4, 16, 17]. Accordingly, spin coating of CeO<sub>2</sub> suspension could be a new way to realize humidity sensors, which must be assessed.

In this paper, we present a new methodology developed in order to deposit by spin coating a CeO<sub>2</sub> thick layer on silicon substrate and the characterization of the film as well as its humidity sensitivity.

We have used an aqueous suspension of grinded CeO<sub>2</sub> particles with a rheological behavior adjusted with carbopol polymer (Ultrez 21 grade, Noveon). This polymer is a hydrophobically modified crosslinked polyacrylate polymer designed to efficiently impart thickening, stabilizing, and suspending properties to a variety of personal care applications. This product self-wets quickly and easily without any mixing required. It also exhibits improved electrolyte tolerance that is interesting for complex formulation. Depending on carbopol concentration and pH solution, the mechanical behaviors range from purely viscous solutions to elastoplastic gels. An extended review of the mechanical characteristics of the carbopol gels has been done by Piau [46].

The aim of this paper is to investigate in a first time the preparation of CeO<sub>2</sub> particles suspensions and their rheological properties, and silicon substrate treatment as well, in order to cover it. In a second time, the goal is to characterize the CeO<sub>2</sub> thick films formed and to study the modification induced by a conventional annealing. Non-annealed and annealed thick layers have been characterized by scanning electron microscopy (SEM) and by Raman spectroscopy. Finally, gold interdigitated electrodes have been deposited on the annealed thick films to realize a capacitive sensor, which has been tested in humidity to determine its sensitivity. The reported results are very promising and highlight that the capacitance increases with relative humidity. To our best knowledge, it is the first time that humidity sensors are fabricated with such technique.

## 2. Experimental

All experiments conducted in this study have been carried out with cerium oxide (99.9% purity) powder manufactured by Alfa Aesar. As powder granulometry is closed to 10  $\mu\text{m}$ , a grinding stage was required for the deposition of thick films on silicon substrate by spin-coating. Effectively, some little uncovered zones can exist on the substrate if the grain size is too large and it is difficult to completely cover the silicon substrate in these conditions. For these reasons, it was imperative to grind it in order to uniformly cover the silicon substrate and to deposit a film thickness inferior to 10  $\mu\text{m}$ . Firstly, the suspension was prepared by using 50 g of  $\text{CeO}_2$  powder, 70 ml of deionized water and 2 ml of Dolapix CA (organic deflocculating agent) in order to form a slurry which is then poured in a bottle containing 470 g of yttria stabilized zirconia balls (1.2 mm diameter). A grinding and mixing stage either 24 or 48 h was operated with a rotary overhead shaker (Reax 20, Heidolph) at 10 rpm. Balls have been then removed and mixing was continuously done to prevent any agglomeration via sedimentation of this raw suspension. Rotation was stopped only for pipetting samples for further batch preparations dedicated to spin-coating deposition. The volume of a batch was fixed to 20 ml and consists in a mix of raw  $\text{CeO}_2$  suspension, deionized water and 24 h hydrated carbopol solution (Ultrez 21 grade, Noveon) at 1% w/w. Because of basic pH of the  $\text{CeO}_2$  suspension, direct swollen of carbopol particles occurs leading to an increase of viscosity and a limited sedimentation. Pipetting volumes (HandyStep electronic, Brand) of each element were adjusted in order to obtain a suspension with different carbopol concentrations ranging from 0 to 0.3% w/w and a fixed  $\text{CeO}_2$  concentration (0.24 g/ml).

As sonication is a common way to break up agglomerates and promote dispersion of particles into base fluids, the batch mixture was dispersed and grounded using an

ultrasonic horn Bandelin Sonopuls HD3200 with a titanium tapered tip KE76. Operating power was set to 40% with a 0.5 s pulse and 0.5 s relaxation cycles applied during 40 s. This maximum admissible amplitude was limited because of the high-density energy dissipation (fluid temperature elevation) and the life duration of the tip considerations (erosion phenomena).

Flow measurements have been carried out at 20 °C with a control stress rheometer (AR1000N, TA Instruments) and a cone-plate geometry (40 mm diameter and 1° angle) in order to determine rheological properties of preparations. The plate of the rheometer was the same silicon substrate used for spin-coating depositions. The silicon wafer (2'') was simply stucked onto the rheometer.

The particle size distribution (PSD) of the grain dispersed in the CeO<sub>2</sub> suspension was characterized by using a Horiba LA-950 laser granulometer.

Type (111) silicon substrates with an 2-20 Ω.cm resistivity was chosen for all experiments. Surface treatment retained was realized either with acetone or a diluted hydrofluoric acid (HF) during 5 minutes, whether for the purpose of spin-coating or for rheometry.

In the first stage of spin-coating process, the mix carbopol-CeO<sub>2</sub> was deposited as a droplet (500 μl) onto the substrate. In the second stage, the substrate was accelerated (5000 rpm/s) to a prescribed rotational speed (3000 rpm) during 30 s. The coating procedure was repeated six times in order to increase the CeO<sub>2</sub> film thickness and to fully cover the substrate. Then CeO<sub>2</sub> layer was first dried on a hotplate at 200 °C during 1 h in order to improve the adhesion of the CeO<sub>2</sub> film on the silicon substrate and to evaporate the water. Then, it was annealed at 1350 °C during 6 h under air atmosphere in a tubular furnace in order to densify the thick film and also to eliminate the carbon compounds.

The thickness of the annealed CeO<sub>2</sub> layer is 6.5 μm and has been measured by using a profilometer.

The morphology of the CeO<sub>2</sub> films was studied by scanning electron microscopy by using Hitachi S3460N and Tescan-Mira equipments and their crystallinity was characterized by using both UV and visible Raman spectroscopy in order to analyze the surface and the bulk.

An InVia Renishaw Raman spectrometer was used in a backscattering configuration at room temperature. The excitation sources used were helium-cadmium and helium-neon lasers with a wavelength of 325 (UV) and 633 nm (visible), respectively. UV and visible Raman spectra of the different samples were performed with 40 X or 50 X objectives, respectively. The position ( $\delta$ ) and the full width at half maximum ( $\Gamma$ ) of the Raman lines were extracted by fitting with Lorentzian and Gaussian model. The measurement dispersion was depending on the slight inhomogeneities of the CeO<sub>2</sub> layers and the accuracy of the spectrometer. It has been estimated from statistical analysis at 0.2 and 0.3 cm<sup>-1</sup> for  $\delta$  and  $\Gamma$ , respectively.

The humidity sensors were made by depositing gold interdigitated electrodes on the top of the CeO<sub>2</sub> thick layer by screen printing technique. The sensors were placed in a Secasi hot/cold oven with a moisture rate regulated from 5 up to 95% at a temperature of 25 °C. The capacitance values of the sensors were measured with an LCR Fluke PM 6306 meter.

### 3. Results and discussion

Typically, particles in suspension used for spinning process are colloidal (20-300 nm) and film thickness is in the order of several hundreds of nanometers [47]. As the raw CeO<sub>2</sub> powder used in this study presents a monomodal distribution of the particle

size centered at 10  $\mu\text{m}$  (Fig. 1), it was imperative to grind it in order to uniformly cover the silicon substrate. The mixing and ball grinding of the  $\text{CeO}_2$  suspension followed by sonication stage lead to a significant particle size reduction as depicted by PSD in Fig. 1.

After a rotary milling of 24 h (Fig. 1-a), the main mode of the PSD is slightly shifted and the PSD becomes broader because of apparition of smaller size particles (lower limit 0.2  $\mu\text{m}$ ) and the existence of non-grounded particles. This observation corresponds to a soft mechanical stripping and debulking of particles, especially considering SEM micrograph of raw particles (Fig. 2-a). The effects of the sonication stage are much more important. The PSD becomes trimodal with a mode corresponding to the original population, which is much less significant and shifted toward 20  $\mu\text{m}$ . The main new mode is centered on 670 nm and is associated to disrupting of mechanically crushed particles and those stressed by the grinding. Smaller particles (80 nm mean size) are also observed but they are a minority. Contrary to the previous milling step, a 48 h period is sufficient to fractionize all the particles of the raw  $\text{CeO}_2$  powder (Fig. 1-b). A bimodal PSD is obtained with two modes observed previously and centered at 580 and 80 nm respectively, with the first one, which predominates. Sonication leads once again to a new particle size reduction. Weak size evolution is observed and particle numbers adjustment is mainly concerned. The 580 nm population decreases (with a slight shift to 510 nm) to the benefit of the one centered at 80 nm. The minimum size, which can be obtained with these operations, seems to be 40 nm and the maximum size still remains important and is 8  $\mu\text{m}$ . It is worth noting that this latter methodology ensures good-reproducibility as highlighted by the PSD obtained with two different batches (Fig. 1-b). For these reasons, the subsequent preparation for spin-coating experiments have been obtained by following this protocol. At least, both smaller modes, 510/670 nm and 80 nm,

are achieved with 24 and 48 h ball milling period but 80 nm species are found only for a grinding period of 48 h. This observation is also shown by SEM micrographs (Figs. 2-b and 2-c). The SEM image of CeO<sub>2</sub> raw powder indicates the 500-600 nm population exists initially in an agglomerated form (Fig. 2-a).

The desired characteristics of spin-coated films include uniformity in thickness and morphology and absence of pinholes and other mechanical defects. Fluid rheology has been reported as an important property impacting film profile [48, 49]. For colloidal suspension, inter-particles forces and local solid fraction drive the shear thinning behavior [49]. Large viscosity changes could thus occur for small changes in concentration due to film spreading as indicated by Regh et al. for non-hard sphere colloidal suspension [47]. For these reasons, the behavior of CeO<sub>2</sub> suspension must be studied by rheological measurements and we have analyzed them in the context of rheological behaviors of two commercial photoresists that are LOR (Microchem) and S1805 (Shipley). These products are known to easily cover a silicon substrate by using spin coating technique and they are commonly used in photolithography process for microelectronic applications. The flow curves (i.e. shear stress versus shear rate data) of photoresists and CeO<sub>2</sub> grinded/sonicated suspension are reported in Fig. 3. The 0.24 g/ml CeO<sub>2</sub> suspension is a low viscous Newtonian fluid (2.3 mPa.s). This viscosity is lower than the viscosity of Newtonian S1805 photoresist (6.7 mPa.s). A more viscous with a low shear thinning behavior is observed for LOR photoresist. We consider the constitutive equation corresponding to the power law model [50]:

$$\tau = K \dot{\gamma}^n$$

where  $\tau$  (Pa),  $K$  (Pa.s),  $\dot{\gamma}$  (s<sup>-1</sup>) and  $n$  (dimensionless) are shear stress, consistency index, shear rate and power law index.

Fitting the data, the values of  $K$  and  $n$  are equal to 0.223 and 0.95, respectively. The power law index is close to 1. This agrees with the low shear-thinning behavior of LOR photoresist. It is interesting to note that the power law index would be equal to 1 if the fluid behavior was Newtonian.

Insofar as rheometric tests concern low viscous fluids and are performed on a rotational rheometer (control torque device), experimental precautions are required. Shear rate range should be adjusted in order to respect the low-torque limit. The air bearing of the instrument allows virtually friction free application of torque but any real air bearing presents internal friction torque, which must be considered for low viscous fluids. The small variations can be mapped as a function of the angular position. This rotational mapping has been realized with software option set to 3 iterations. Fluid surface tension should not produce a torque in rotational rheometers based on the idealized assumption of rotational symmetry. Recently, it has been demonstrated that this principle could be infringed because finite deviation of the contact line symmetry and fluid/geometry interface angle symmetry can produce a significant torque in case of low viscous fluids [51]. Sample loading and proper sample volume must be carefully set to control as much as possible the contact line. For our experiments, best practices leading to a pure Newtonian response have been found by using low viscous standard silicon oil and micropipette. All the data reported in Fig. 3 correspond to a silicon substrate systematically degreased with acetone before each test.

Another important phenomenon to pay special attention concerns the sedimentation because it will directly influence the uniformity of spinning films and affect rheometric tests. As settling time of  $\text{CeO}_2$  particles is short enough, rheometric tests consist in a fast decreasing shear rate sweep starting with fluid highly sheared during

2 min. As the impact of inertia contribution becomes then significant for low viscous fluids, the inertia instrument correction has been applied.

Considering rheological behavior of raw CeO<sub>2</sub> suspension and sedimentation, it is imperative to increase the viscosity of the CeO<sub>2</sub> suspension up to the range of photoresists and to stabilize particles while limiting the shear-thinning behavior.

For this purpose, Carbopol Ultrez 21 was selected and three mass concentrations have been studied to prepare fluids dedicated to spin coating process. Rheometric tests were carried out immediately following fluid preparation (Fig. 3).

We can see that all systems present a shear-thinning behavior and moreover, the increase of the viscosity depends directly on carbopol mass. Both 0.15 and 0.2% carbopol concentration show an evolution in logarithmic scale suggesting that there is no surface tension effect and this true shear-thinning behavior could be fit with the power law model. We can also note that their rheological behaviors become similar for the high shear rate indicating that the system behaves as non-interacting CeO<sub>2</sub> particles flowing in a media with a constant viscosity. The 0.3% carbopol concentration highlights a viscosity level more important and the non-Newtonian behavior is more pronounced. Moreover, the low shear rate deviation (below 1 s<sup>-1</sup>) indicates surface tension torque effect.

Nevertheless, it is important to note that the silicon substrate is perfectly covered when the LOR and S1805 photoresists are deposited by spin-coating while they have a shear thinning and Newtonian behaviors, respectively. For these reasons, the carbopol concentration of 0.3% has been excluded for spin coating experiments and the 0.2% carbopol concentration has been retained because the silicon substrate seems better covered in comparison with 0.15 carbopol concentration.

Furthermore, as the silicon substrate needs a hydrofluoric acid treatment before

the deposition in order to etch the native oxide layer, which can exist, this hydrophobic surface has been used to study the rheological effects even if this confined flow can't give further indication of quality deposition by spin-coating. However, the rheological behavior of the CeO<sub>2</sub> suspension with a carbopol concentration of 0.2% after a HF treatment has been compared with that after an acetone treatment because the previous studies were done after an acetone treatment, as in Fig. 3 for example.

Thus, we can see that the rheological curves concerning the CeO<sub>2</sub> suspension with a 0.2% carbopol concentration after an acetone treatment or after a HF treatment are located between the LOR photoresist and S1805 photoresist curves, as shown in Fig. 4. Moreover, flow curves for fluid with 0.2% carbopol concentration realized with a new grinded/sonicated batch show that same shear thinning behavior is observed for shear rate higher than 1 s<sup>-1</sup>. No surface tension effect is still observed for the silicon substrate degreased whereas low shear rate plateau appears for the HF treatment. This suggests that interface angle is affected. It could be also wall slip through changes in fluid-surface interactions. Indeed, hydrophobic surfaces allow noticeable slip because of small dipole moment of polar liquids [52] and nanobubbles at solid-liquid interface [53].

Thus, fluid-surface interactions seem to be determinant for deposition scenario. Regh et al. interestingly remark that local charge distribution on the substrate may influence film structure and film thinning for suspension [47]. A theoretical approach of particle transport and aggregation assuming a Newtonian behavior in a spin-coating process highlights that adhesive properties of the particles and substrate influence the deposition process [54].

In summary, it is difficult to affirm that the HF treatment is clearly better than acetone treatment for the CeO<sub>2</sub> suspension deposition by spin-coating. However, we think

that the quality of the Si/CeO<sub>2</sub> interface should be better if the native oxide layer was etched before the deposition. We have observed that the adhesion of CeO<sub>2</sub> nanoparticles on the silicon substrate is better after a HF acid treatment than after an acetone treatment. The reproducibility of the technological process using the HF acid treatment is also better than that using the acetone treatment. Thus, we have decided to clean the silicon surface with the HF treatment before the deposition of thick layers.

Thick CeO<sub>2</sub> layers have been deposited by spin-coating with the 0.2% carbopol suspension and HF treated silicon substrate. Then, after a drying stage at 200 °C, the CeO<sub>2</sub> layers have been annealed at 1350 °C for 6 h under air atmosphere. The morphology and the crystallinity have been characterized by scanning electron microscopy and Raman spectroscopy. SEM micrographs of CeO<sub>2</sub> thick layers before and after an annealing performed at 1350 °C during 6 h under air atmosphere are shown in Fig. 5. An increase in CeO<sub>2</sub> grain size has been observed after annealing. Moreover, the presence of pores has also been highlighted with the non-annealed (Fig. 5-a) and annealed CeO<sub>2</sub> layer (Fig. 5-b) but the pores seem more visible after annealing.

Then the CeO<sub>2</sub> thick films were analyzed by visible Raman spectroscopy in order to analyze the layer crystallinity. In fact, the position, the line width, the line shape, and the intensity of the Raman peaks are depending on the vibrational state of the studied material and therefore  $\delta$  and  $\Gamma$  of the Raman band are impacted by the stress state, the crystalline quality and the measurement temperature. Effectively, a fine  $\Gamma$  has stood for a good material crystalline quality.

Fig. 6 presents the visible Raman spectra of a CeO<sub>2</sub> thick film deposited on a (111) Si substrate by spin-coating before and after a post-annealing performed at 1350 °C for 6 h under air atmosphere.

Before annealing, two separate Raman bands are highlighted at 465.5 and 521.4  $\text{cm}^{-1}$  that are the signatures of the triply degenerate Raman active mode of the  $\text{CeO}_2$  thin film [55] and to the longitudinal optical mode of the Si substrate [56], respectively. In this visible Raman spectrum, the  $F_{2g}$  Raman band is attributed to the cubic fluorite phase [57, 58]. After the annealing, the Raman line related to  $\text{CeO}_2$  thick film increases from 465.5 up to 466.2  $\text{cm}^{-1}$  and the  $\Gamma$  of Raman peak related to  $\text{CeO}_2$  layer decreases from 9.5 down to 8.3  $\text{cm}^{-1}$ . Then these values are compared with those obtained with a  $\text{CeO}_2$  powder considered like a stress-free material and taken as a reference ( $\delta = 465 \text{ cm}^{-1}$ ,  $\Gamma = 8.2 \text{ cm}^{-1}$ ) [59] in order to analyze the impact of post-annealing on the  $\text{CeO}_2$  layer crystallinity. Thus, we note that  $\Gamma$  is close to the reference that confirms a good crystalline quality of the post-annealed  $\text{CeO}_2$  films. However, the Raman position is clearly superior to the reference value. This is explained by a compressive strain in relation to the Si substrate [60]. Moreover, the  $\text{CeO}_2$  layers have been characterized by UV Raman spectroscopy because the low penetration depth (close to 30 nm) of the UV radiation into the material allows to obtain a Raman signal coming from the  $\text{CeO}_2$  layer and not from the silicon substrate [57]. For these reasons, non-annealed and annealed  $\text{CeO}_2$  films have also been characterized by UV Raman spectroscopy with a laser wavelength of 325 nm. Moreover, the gap value of the band gap energy for a  $\text{CeO}_2$  film [61, 62] is analogous to the excitation energy and therefore it is possible to observe the resonance Raman effects. In these conditions, the multi-phonon scattering is activated and multi-order Raman modes are present in the Raman spectra [60].

Fig. 7 shows that UV Raman spectra of  $\text{CeO}_2$  thick films before and after annealing are different. In fact, we can observe five Raman lines located at values close to 464.3, 586.5, 1172.4, 1555.2, and 1755.6  $\text{cm}^{-1}$  for the annealed  $\text{CeO}_2$  layer but no

Raman line centered at  $586.5 \text{ cm}^{-1}$  was observed on the Raman spectrum of non-annealed  $\text{CeO}_2$  film. So, the Raman line located at  $464.3 \text{ cm}^{-1}$  is ascribed to the triply degenerate Raman active mode ( $F_{2g}$ ) of the  $\text{CeO}_2$  thin film [55] and those found at  $1172.4$  and  $1755.6 \text{ cm}^{-1}$  can correspond to a second-order longitudinal optical mode (2LO) and to a third-order longitudinal optical mode (3LO), respectively [55, 58, 59, 63]. The small Raman line located at  $1555.2 \text{ cm}^{-1}$ , meanwhile, is attributed to a band related to physisorbed  $\text{O}_2$  [64]. However, the identification of the Raman line located at  $586.5 \text{ cm}^{-1}$  is more difficult because this broad band is attributed to a disorder band, which is generally named D [58, 59, 65]. Moreover, we have already studied the origin of D band by UV Raman spectroscopy in a previous paper [66], and we have highlighted that the D band was originated from the combination of two bands which are attributed to the presence of oxygen vacancies and of  $\text{Ce}^{3+}$  ions in  $\text{CeO}_2$  thin layer, respectively. So, we can affirm that the Raman band centered at  $586.5 \text{ cm}^{-1}$  is attributed to the presence of oxygen vacancies and  $\text{Ce}^{3+}$  ions in  $\text{CeO}_2$  thick layer deposited on silicon substrate by spin coating. Effectively, the emergence of oxygen vacancies in a  $\text{CeO}_2$  layer can be correlated with the reduction of  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$  [65, 67].

As for the characterization done by visible Raman spectroscopy, we can note that the annealing has also induced a decrease in the  $F_{2g}$  Raman peak linewidth from  $48.3$  down to  $11.4 \text{ cm}^{-1}$ , which is induced by an improvement of the  $\text{CeO}_2$  layer crystallinity. These results are confirmed by the presence of the multi-phonon Raman structures of the third order in the UV Raman spectrum before and after the annealing, that confirms a good crystallinity of the  $\text{CeO}_2$  thick layer in the two cases [68]. For these reasons, we cannot consider that the reduction in  $\Gamma$  is only induced by an improvement of the

crystallinity of the CeO<sub>2</sub> thick layer because  $\Gamma$  also depends on the crystallite size [55].

In fact, the evolution of  $\Gamma$  versus the crystallite size ( $D$ ) is given by the following relation:

$$\Gamma = a + \frac{b}{D}$$

where  $a$  and  $b$  are constants depending of the material and the unit of  $\Gamma$  and  $D$  are cm<sup>-1</sup> and nm, respectively.

In these conditions, we can say that the reduction in  $\Gamma$  is explained by the improvement of the crystallinity of the CeO<sub>2</sub> layer and/or by an increase in the crystallite size as shown in Fig. 5. Moreover, the annealing has involved the apparition of oxygen vacancies and Ce<sup>3+</sup> ions in the film. We think that the annealing involves the reaction between the silicon substrate and the CeO<sub>2</sub> layer that implies the creation of oxygen vacancies and the Ce<sup>4+</sup> to Ce<sup>3+</sup> cations transformation. Indeed, it is known that oxidized silicon and/or an amorphous silicide layer appears after an annealing done at high temperature. These interfacial reactions occur simultaneously with a reduction of Ce<sup>4+</sup> to Ce<sup>3+</sup> [69, 70].

It is important to specify that the measurements by Raman spectroscopy have been done in many areas on the thick layers and all the results obtained from Raman spectra are reproducible and highlight that the CeO<sub>2</sub> layer is homogeneous.

In order to evaluate the humidity sensing characteristics of the CeO<sub>2</sub> thick film, gold interdigitated electrodes have been deposited on the top of the CeO<sub>2</sub> thick layer (as shown in the inset in Fig. 8) by screen printing technique. The capacitance ( $C$ ) measurements have been done at a frequency of 200 Hz at a temperature of 20 °C.

Fig. 8 presents the evolution of the sensor capacitance versus the relative humidity. In fact, the capacitance varies slightly from 0.9 up to 1.2 nF when RH rises from 5 up to 25%. Then  $C$  increases sharply from 1.2 up to 63 nF when RH changes from

25 up to 93%. Moreover, the value of C is nearly recovered when RH drops from 93 down to 5%, as shown in Fig. 8. It is important to note that the capacitance is intimately linked to the dielectric coefficient of the sensing material and consequently to its polarization properties. So, a rise of the relative humidity induces an increase in the adsorbed water molecules onto the sensing material surface, and consequently the polarization is stronger and the dielectric coefficient and capacitance are higher [71]. Besides a low change in the capacitance is observed in the low RH range in Fig. 8 because few water molecules are adsorbed onto the surface of sensing CeO<sub>2</sub> material, that involves a weak polarization and accordingly a low capacitance. For higher RH, the adsorbed water molecules concentration is more important and therefore the polarization is stronger and the capacitance higher [72]. Moreover, the capacitance depends on both dielectric constants of CeO<sub>2</sub> layer and of water. Effectively this phenomenon can also explain the increase in capacitance with the relative humidity. In fact, the dielectric constant of the water (80 [72]) is clearly higher than that of CeO<sub>2</sub> layers (26 [73]). So, we can think that the pores existing in the CeO<sub>2</sub> film fill with water molecules as the RH increases which induces an increase in capacitance [72]. We can add that the high relative humidity water vapor starts to condense in the pores of the CeO<sub>2</sub> layers by capillary effect, even when the partial pressure in the vapor is below saturation. Therefore, we can assume that the water vapor condensation in the pores induces an increase in capacitance as it has been already observed with porous silicon layer [12] and amorphous Al<sub>2</sub>O<sub>3</sub> nanotubes [72].

The presence of oxygen vacancies in the CeO<sub>2</sub> thick layer can also be a factor impacting the humidity sensitivity as highlighted for ZrO<sub>2</sub> nanorods [30]. In these conditions, the oxygen vacancies can act as highly active sites for water adsorption. This phenomenon is consistent with our CeO<sub>2</sub> layer characterization by UV Raman

spectroscopy because we have highlighted the presence of oxygen vacancies in the annealed thick films. In summary, the humidity sensitivity is explained by an increase in the dielectric constant of CeO<sub>2</sub> thick layer and by the presence of oxygen vacancies in the CeO<sub>2</sub> thick layer.

#### 4. Conclusion

In this paper, we have presented a new technique in order to deposit a CeO<sub>2</sub> thick film on a (111) silicon substrate. To our knowledge, it is the first time that such technique is reported. Firstly, a suspension done from CeO<sub>2</sub> powder, Dolapix and deionized water is grinded by a rotary milling for 48 h and then by a sonication for 40 s in order to decrease the CeO<sub>2</sub> particle size. Secondly, 0.2% of carbopol polymer has been added to adjust the viscosity of the suspension. The carbopol polymer concentration has been chosen on the basis of rheometric characterization results. Thirdly, the CeO<sub>2</sub> suspension adjusted with the carbopol polymer has been deposited by spin-coating and annealed at 1350 °C for 6 h under air atmosphere. A good crystallinity of annealed film has been highlighted by Raman spectroscopy but the presence of oxygen vacancies has been observed. A humidity sensor has been done on the CeO<sub>2</sub> thick film and we have shown that the capacitance increases from 0.9 up to 63 nF when the relative humidity changes from 5 up to 93%. These first results are very promising because this humidity sensor has been performed by using a new and low-cost technique. Of course, this original method needs to be optimized in order to improve the performances of the sensor but the aim of this paper is to present a new technique to realize a low-cost humidity detector. This technique can also be used in order to realize other types of sensors using other materials.

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## **FIGURE CAPTIONS**

Fig. 1: Influence of rotary grinding and sonication on the particle size distribution of the CeO<sub>2</sub> suspension for a grinding time of 24 h (Fig. 1-a) or 48 h (Fig. 1-b).

Fig. 2: SEM micrographs before grinding (2-a), after a rotary milling of 24 h and a sonication (2-b) and after a rotary milling of 48 h and a sonication (2-c).

Fig. 3: Rheological behaviors of CeO<sub>2</sub> suspension without carbopol and with a carbopol mass concentration of 0.15, 0.2 and 0.3%, LOR photoresist and S1805 photoresist.

Fig. 4: Rheological behaviors of S1805 and LOR photoresists, CeO<sub>2</sub> suspension with a viscosity adjusted with 0.2% carbopol polymers concentration on the silicon substrate treated with acetone or hydrofluoric acid.

Fig. 5: SEM micrographs of CeO<sub>2</sub> layers before and after an annealing performed at 1350 °C for 6 h under air atmosphere.

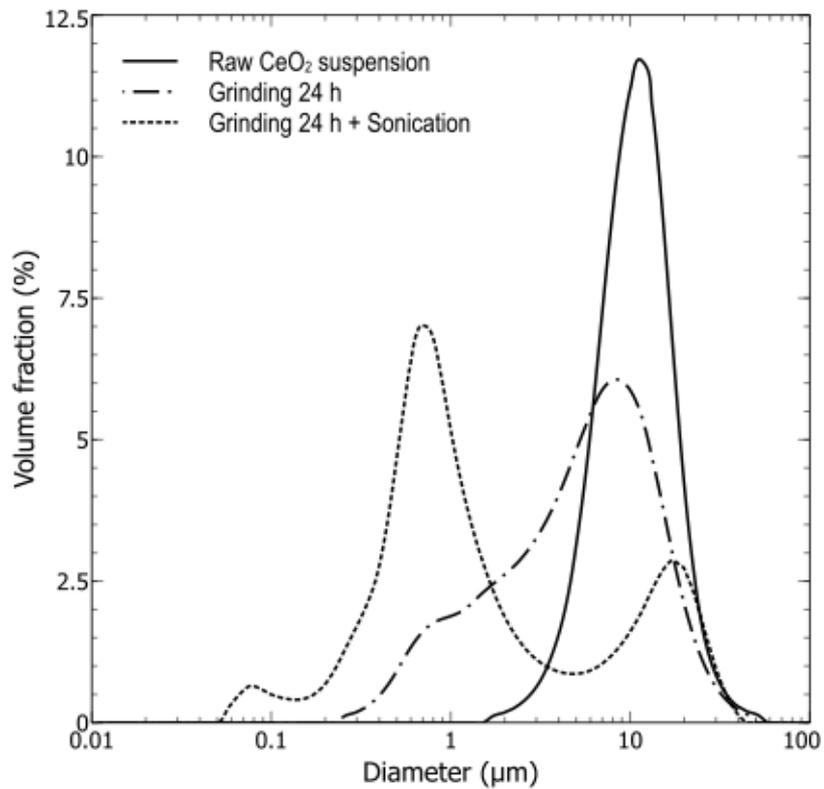
Fig. 6: Raman spectra of CeO<sub>2</sub> thick film deposited by spin coating on a (111) Si substrate before and after an annealing performed at 1350 °C for 6 h under air atmosphere. Raman spectra were obtained with a laser wavelength of 633 nm. The inset is a zoom of the spectra.

Fig. 7: Raman spectra of CeO<sub>2</sub> thick film deposited by spin coating on a (111) Si substrate before and after an annealing performed at 1350 °C for 6 h under air atmosphere. Raman spectra were obtained with a laser wavelength of 325 nm.

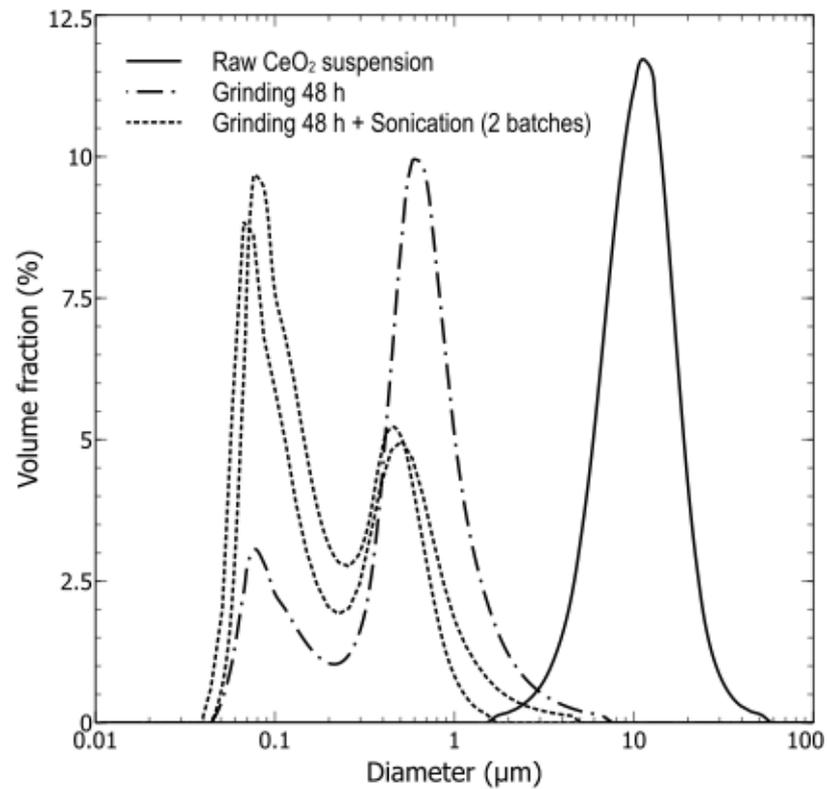
Fig. 8: Influence of the relative humidity on the capacitance of a sensor performed on a CeO<sub>2</sub> thick layer deposited by spin coating on a silicon substrate. The square is the

value of the capacitance obtained after the humidity exposure. The inset is a schematic representation of the sensor.

**Figure 1**



**1-a**



**1-b**

# Figure 2

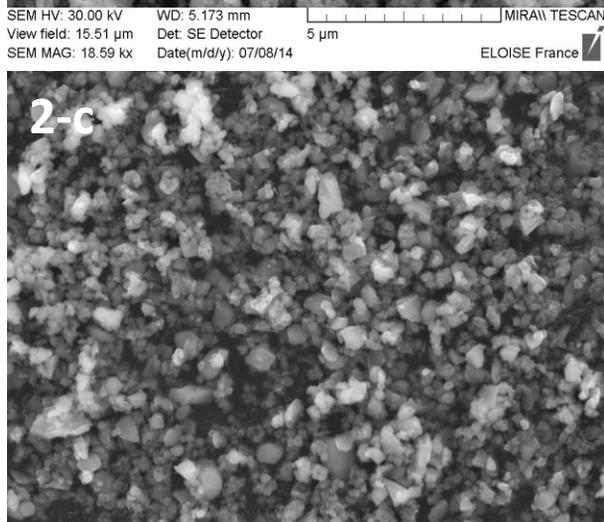
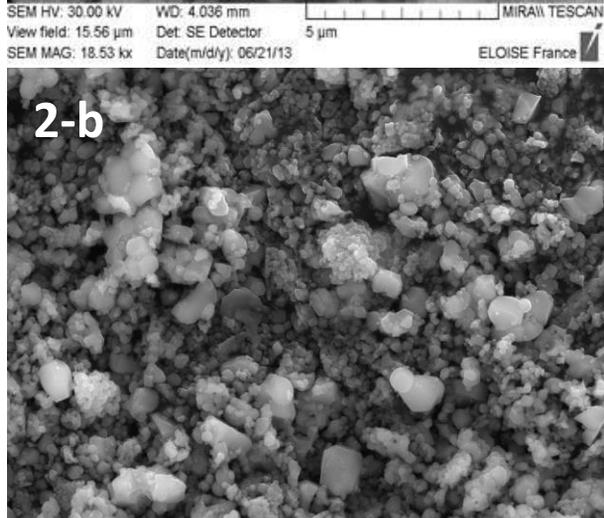
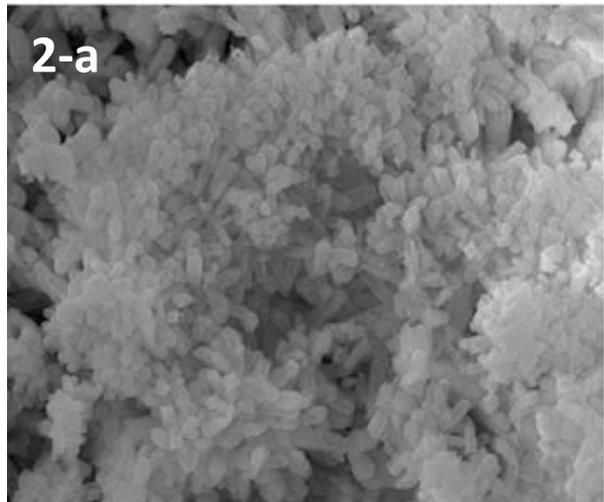


Figure 3

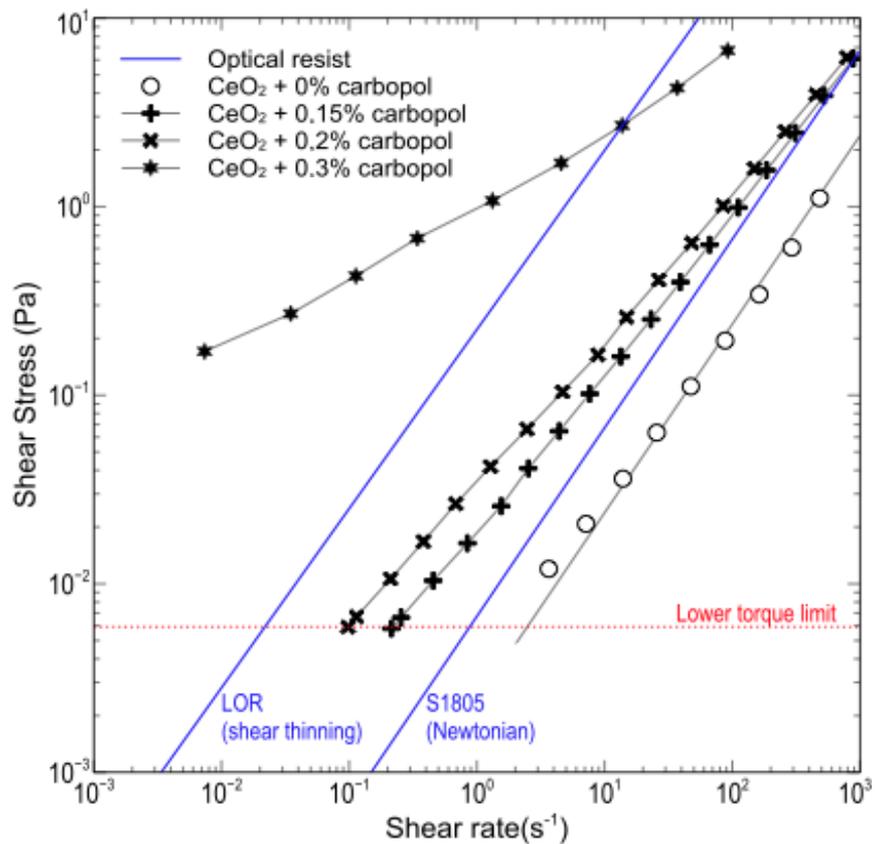
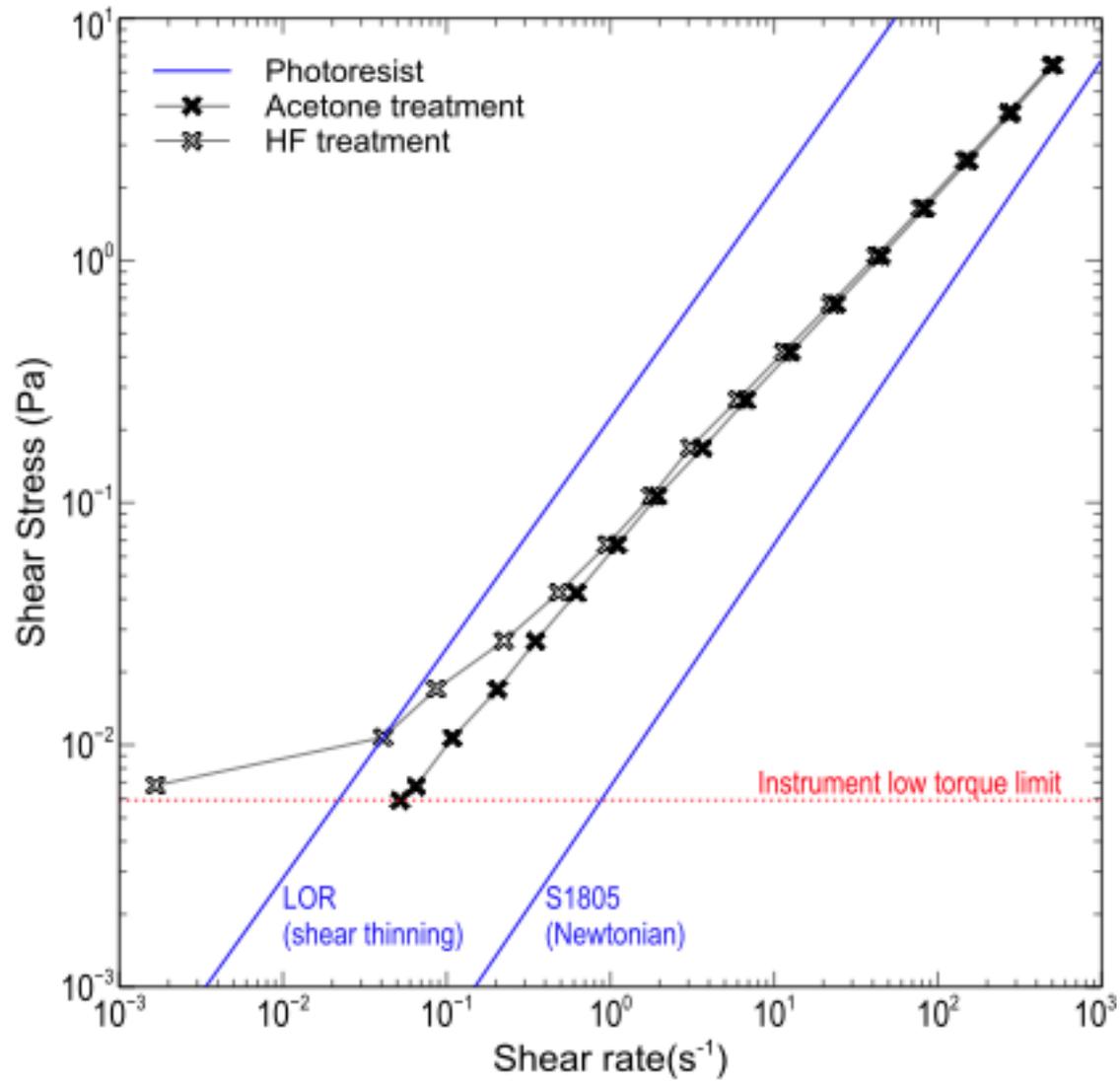


Figure 4



**Figure 5**

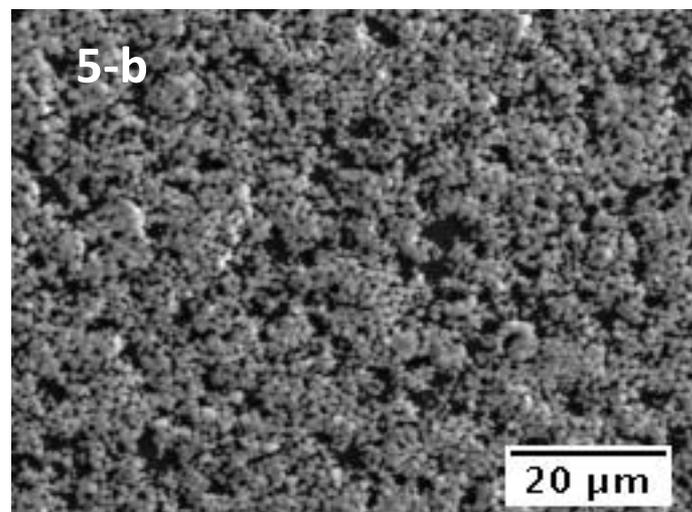
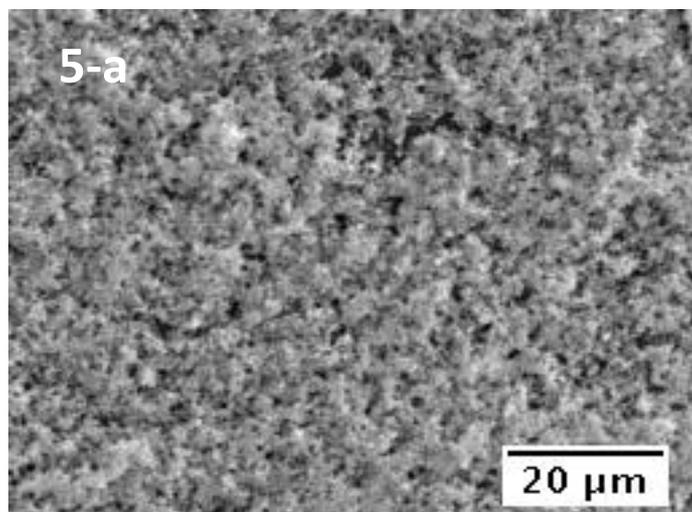


Figure 6

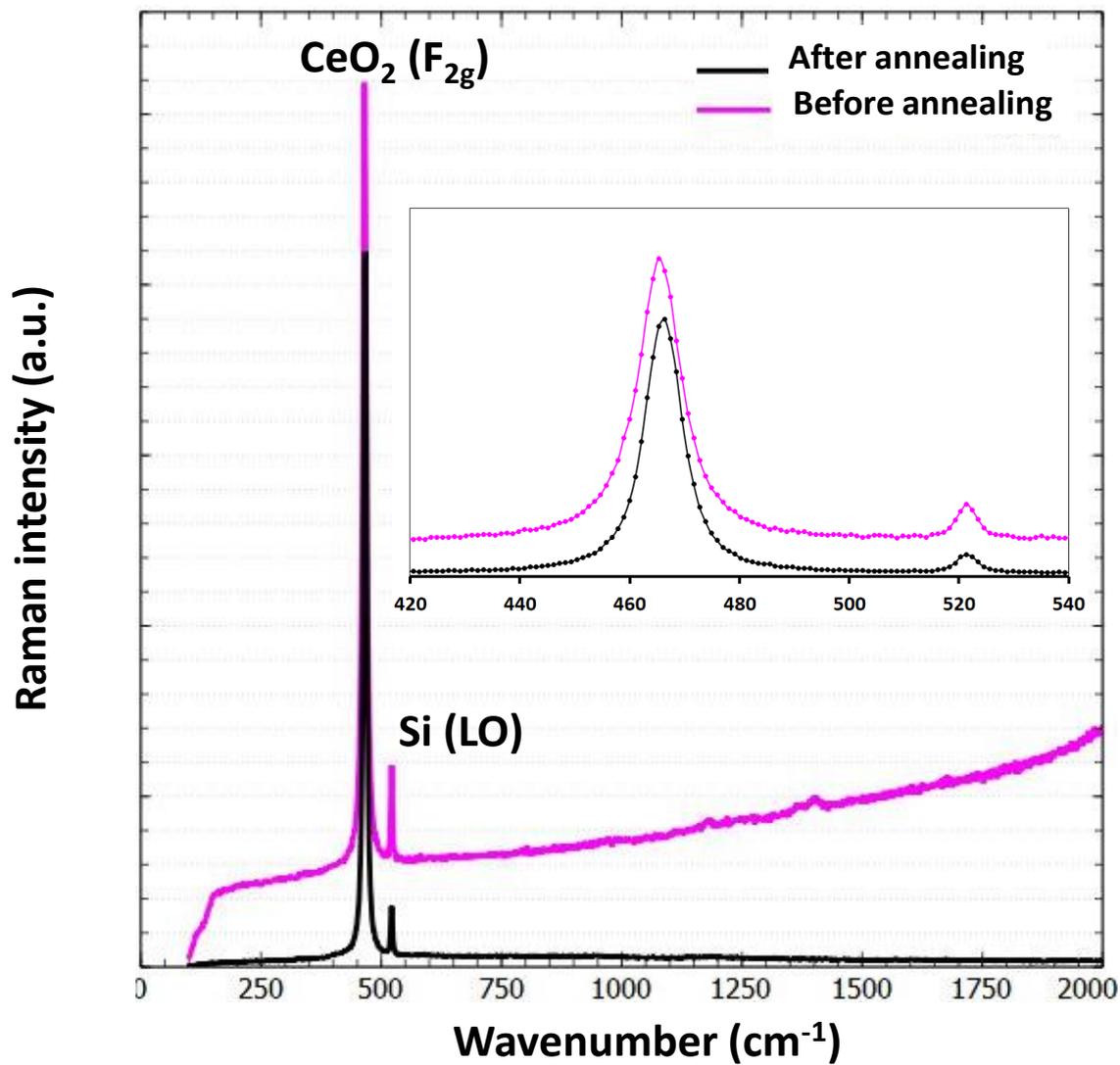


Figure 7

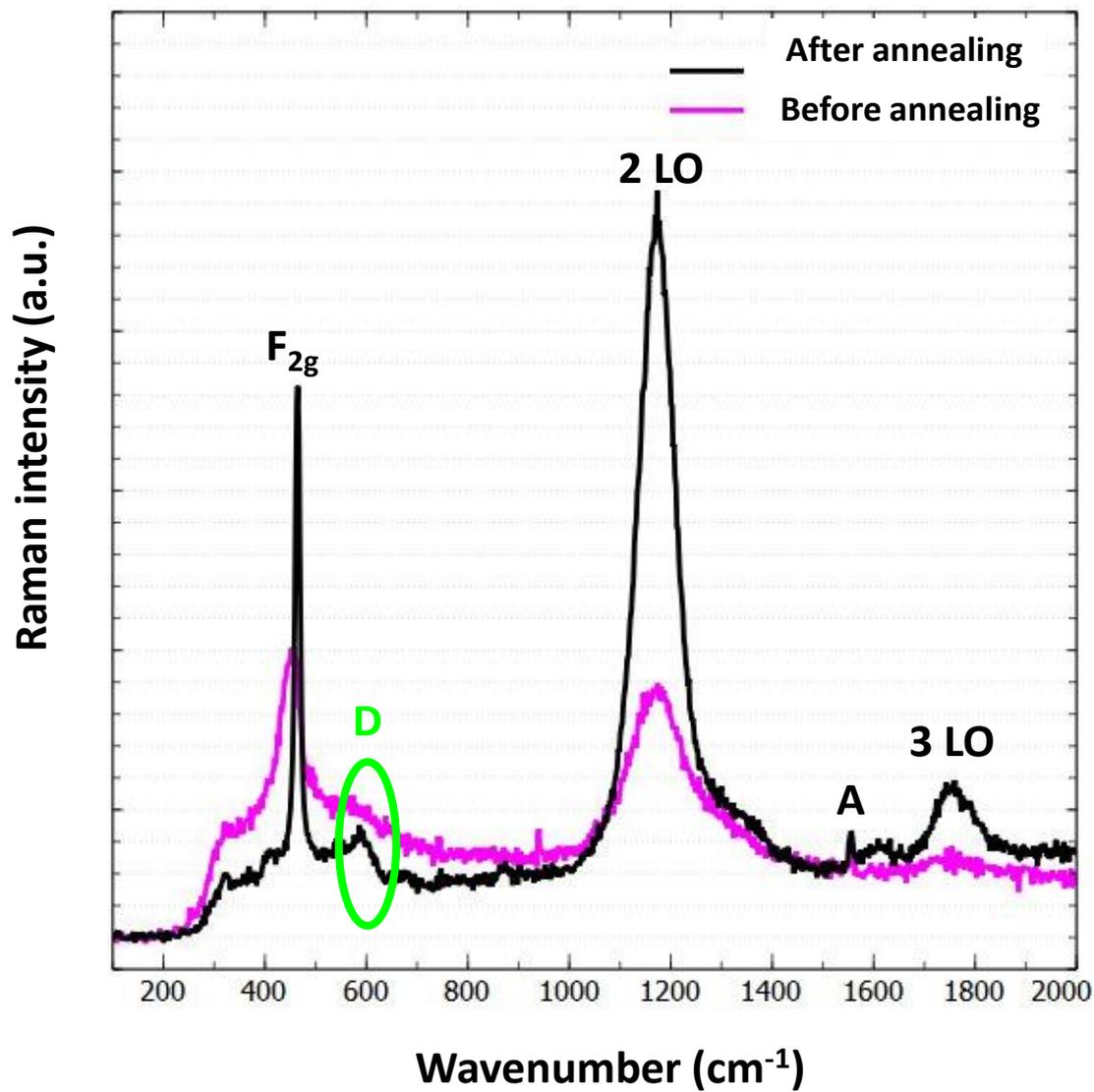
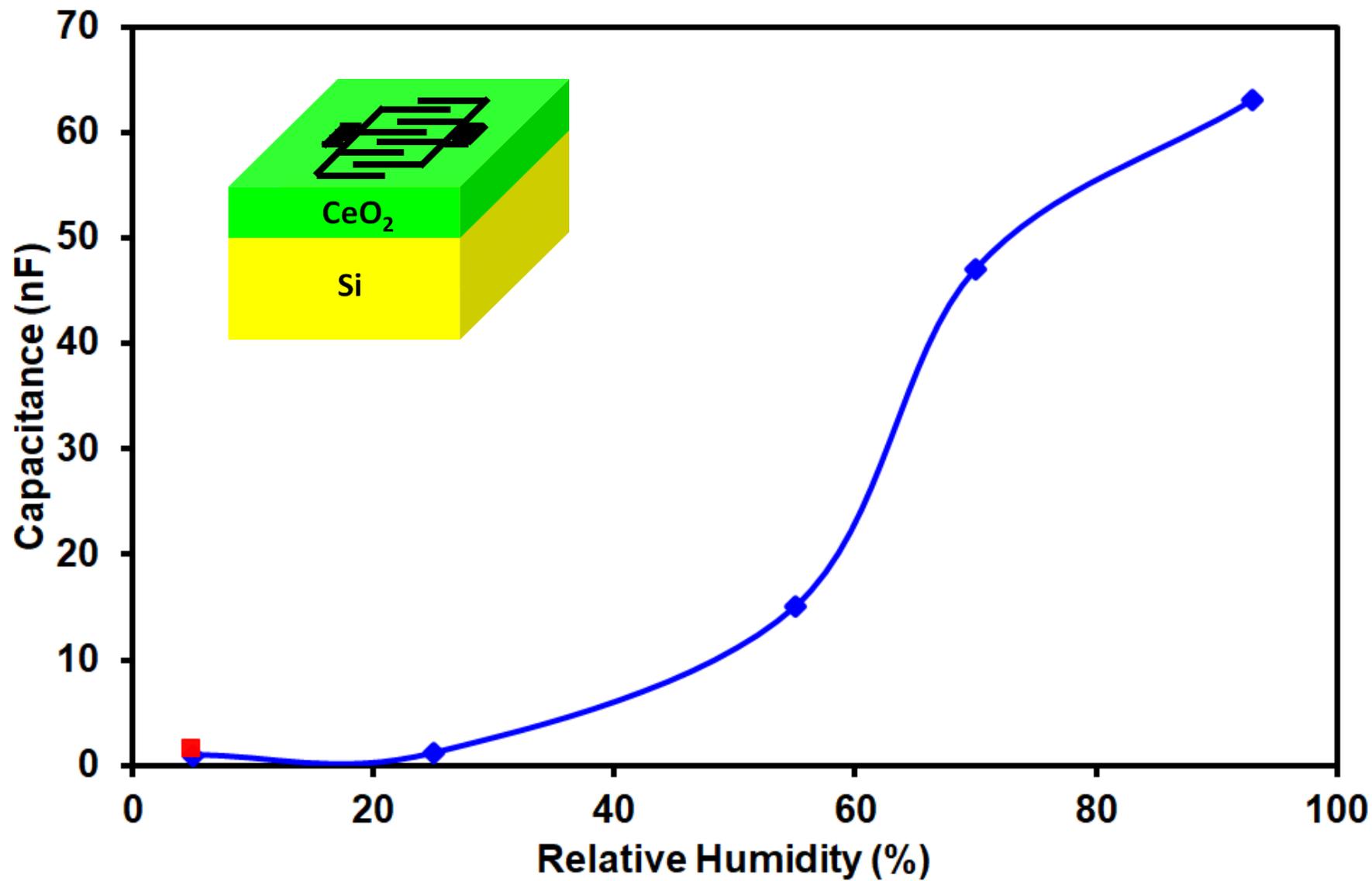
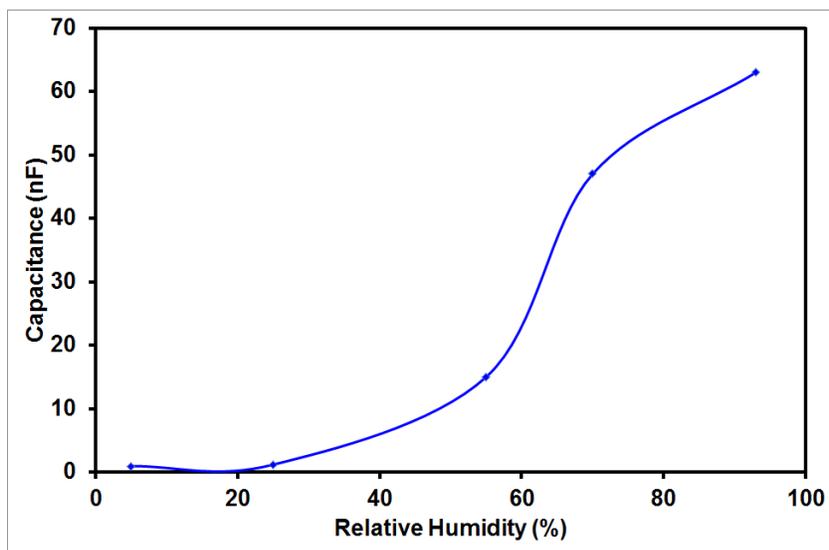


Figure 8





**This figure presents the impact of the relative humidity on the capacitance of a sensor performed on a CeO<sub>2</sub> thick layer deposited on a silicon substrate by using a new process of deposition from a suspension of CeO<sub>2</sub> nanoparticles. First promising results on the humidity sensitivity have been shown.**