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Full Length Research Paper

Low temperature synthesis of La_2O_3 and CrO_2 by Sol – Gel process

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Some issues such as tunneling, leakage current and light atom penetration through the film are threatening the ultra thin SiO_2 be as a good dielectric for future industrial and electronic devices and in ceramic technologies. A series of experiments to synthesis La_2O_3 as well as CrO_2 has been done at low temperature with using sol-gel method. The nano structural properties of La_2O_3/CrO_2 equipped with 5 to 40 nm size are investigated. The obtained results show the potential of La_2O_3/CrO_2 for not only for lowering the interface – state density, but also as a good dielectric for the future of nano electronic. These structures have been studied by using XRD (x ray diffraction) technique and X- powder method.

Key words: Nano structures, La_2O_3, Gate dielectric, x-powder method and sol-gel method.

INTRODUCTION

The gate SiO_2 dielectric thickness in current complementary metal oxide semiconductor (CMOS) transistors is less than 1 nm. It is mostly interface and so thin film cannot obviously prevent leakage, tunneling currents and boron diffusion (Morgen et al., 2006; Bahari et al., 2005; Morgen et al., 2005; Bahari et al., 2006, 2006b; Morgen et al., 2007; Bahari et al., 2008). The higher K- gate dielectric materials can thus be introduced as the alternative gate dielectrics for future of CMIS (I: insulator) devices. La_2O_3 has largest band gap of the rare earth oxides at 4.3 eV, while also having the lowest lattice energy, with very high dielectric constant, $\varepsilon = 27$. It is widely used in industry as well as in the research laboratory. Moreover, the La_2O_3/CrO_2 gate stacks with high electrical permittivity show an amorphous structure of low temperature which can be used instead of ultrathin silicon dioxide gate dielectric in current CMOS devices (Duan et al., 2008; Alexazder et al., 2006; Dercz et al., 2006) due to its excellent chemical properties (Dercz et al., 2006; Zhu, 1998; Kurzweg et al., 1998; Betz et al., 1999) and independent La_2O_3 network within the CrO_2 network. However, La_2O_3 has p-type semi-conducting properties because its resistivity decreases with an increase in temperature, average room temperature resistivity is 10 kΩ·cm (Kale et al., 2005).

In this work, we have synthesized La_2O_3/CrO_2 which is suitable for CMIS. Different crystalline forms of lanthanum oxide have been prepared. At low temperatures, La_2O_3 has an A-M_2O_3 hexagonal crystal structure (Kale et al., 2005). Its crystalline phase can be used for the potential applications of the ceramic – mesoporous structures, as an ingredient for the manufacture of piezoelectric and thermoelectric materials, automobile exhaust-gas converters contain La_2O_3 (Cao et al., 2005). La_2O_3 is also used in X-ray imaging intensifying screens, phophors as well as dielectric and conductive ceramics. We have demonstrated to synthesis of hexagonal crystal phase (h-La_2O_3) at room temperature by using Sol-gel method. Some researchers (Wells, 1984; Wyckoff, 1963; Vinogradova et al., 2004; Manoilova, 2004) believe that the La^{3+} metal atoms are surrounded by a 7 coordinate group of O^{2-}atoms, while the oxygen ions are in an octahedral shape around the metal atom, we see there is one oxygen ion above one of the octahedral faces. In contrast to low temperature case, at high temperatures the La_2O_3 converts to a C-M_2O_3 cubic crystal structure. The La^{3+} ion is surrounded by a 6 coordinate group of O^{2-} ions. However, La_2O_3 in ferroelectric materials content has still needed to be studied due to its structural collapse during formation of the mesoporous phase and its phase transformation from hexagonal crystal phase

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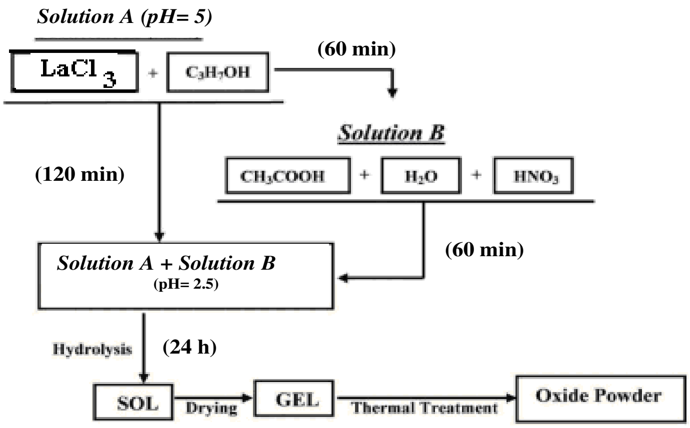

Figure 1. Preparation steps of La_2O_3 powders. Similar procedure is for CrO_2.

to cubic crystal phase (Pajak et al., 2003; Duan et al.,2008; Alexazder et al., 2006; Dercz et al., 2006).

For this reason, we synthesize CrO_2 nanoparticles in parallel to La_2O_3 nanoparticles in this structure and the obtained results indicate the potential applications of the present combination.

Experimental procedure and details

Lanthanum dioxide was prepared by the hydrolysis and condensation of $LaCl_3$ used as precursor under acidic conditions. In this process, a 0.1 M solution of $LaCl_3$ is sprayed onto a preheated substrate. We got two ways to control hydrolysis rate which can be viewed as occurring in hydrolysis followed by dehydration:

$2\ LaCl_3 + 3\ H_2O \rightarrow La(OH)_3 + 3\ HCl$
$2\ La(OH)_3 + heat \rightarrow La_2O_3 + 3\ H_2O$

On the other hand, hexagonal La_2O_3 involves precipitation of nominal $La(OH)_3$ from aqueous solution using a combination of 2.5% NH_3 and the surfactant sodium dodecyl sulfate followed by heating and stirring for 24 h at 80°C (Vinogradova et al., 2004):

$2\ LaCl_3 + 3\ H_2O + 3\ NH_3 \rightarrow La(OH)_3 + 3\ NH_4Cl$
$LaCl_3 \cdot 3H_2O \rightarrow La_2O_3$

Other routes include:

$2\ La_2S_3 + 3\ CO_2 \rightarrow 2\ La_2O_3 + 3\ CS_2$
$2\ La_2(SO_4)_3 + heat \rightarrow 2\ La_2O_3 + 6\ SO_3$

Thus the kinetic is conditioned and it is becoming possible. The water amount necessary to the hydrolysis can be chemically controlled with the hydrolysis in order to decrease its reactivity. The precursor can then be hydrolyzed with a small amount of water produced *in situ* by an esterification reaction resulting of the two points: Depending on the pH of the compound, different crystal structures can be obtained. La_2O_3 is hygroscopic; under atmosphere, lanthanum oxide absorbs moisture over time and converts to lanthanum hydroxide (Manoilova, 2004). It is worth noting that there are some reactions as well:

$$C_2H_5OH + CH_3COOH \Leftrightarrow H_2O + CH_2COOC_2H_5$$
$$C_2H_7OH + CH_3COOH \Leftrightarrow H_2O + CH_3COOC_2H_7$$

We have chosen the Sol–gel process to obtain a gel and privileging at maximum of connection formation La -O- La. The overall hydrolysis and condensation reactions are illustrated below:

Hydrolysis

$$\mathrm{La(OR)_3OR} + H_2O \rightarrow \mathrm{La(OR)_3OH + ROH}$$

Condensation

$$\mathrm{La(OR)_3OH + La(OR)_3OR \rightarrow (OR)_3La\text{-}O\text{-}La(OR)_3 + ROH}$$

Or

$$\mathrm{La(OR)_3OH + La(OR)_3OH \rightarrow (OR)_3La\text{-}O\text{-}La(OR)_3 + H_2}O$$

Where $OR = \mathrm{OC}_3H_7$. The chemically controlled condensation of lanthanum alkoxide leads to stable colloidal solutions of monodispersed lanthania nanoparticles.

The La_2O_3 sol was prepared from a lanthanum alkoxide precursor (Betz et al., 1999; Kale et al., 2005; Cao et al., 2005; Wells, 1984; Wyckoff, 1963) lanthanum propoxide (Aldrich), acetic acid (sigma-aldrich) was used as a chelating agent to lanthanum propoxide and isopropanol (sigma-aldrich) as a solvent. To reduce the viscosity of the alkoxide and reactivity with moisture, the alkoxide solution was prepared by stirring lanthanum propoxide and isopropanol at room temperature in the molar ratio 1 La:15 isopropanol. Catalyst solution was with the molar composition of 1.0 H_2O:0.6 HNO_3:7.5 isopropanol was prepared using distilled water, nitric acid (sigma- A ldrich) and isopropanol. Acetic acid was added drop – wise to the stirred alkoxide solution until the molar ratio of acetic acid to La became 2.0, and the solution was kept stirring for 2 h to let complete the reaction between alkoxide and acetic acid. The catalyst solution was mixed with the aforementioned solution to produce a lanthania sol until the molar ratio of La:CH_3COOH:HNO_3:H_2O:C_3H_7OH became 1.0;2.0:1.2:2.0:30 and was then kept stirring for 2 h. The scheme of preparation is illustrated in Figure 1. Similarly, we can synthesize the nano scale CrO_2 and add it into La_2O_3 (Figures 2 and 3).

The properties of Lanthania forms of higher symmetry are very often preferable to cubic one. CrO_2 is usually used as the stabilization component of higher symmetry lanthania (Betz et al., 1999; Cao et al., 2005; Wells, 1984; Wyckoff, 1963; Vinogradova et al., 2004; Manoilova, 2004). Figure 2 shows the XRD patterns of La_2O_3 without CrO_2. As can be seen in Figure 2 (c) peaks at 13°, 24°, 29 to 31° and 44° attributed to the (111), (200), (220) and (311) diffraction planes of the hexagonal lanthania and some cubic lanthania peak at 50 to 80°C. Figure 3 displays the XRD pattern La_2O_3 with CrO_2 (the presence of CrO_2 (50 wt%) in La_2O_3). The new peaks in comparison to Figure 2, attributed to CrO_2 phases. Phase beside of cubic, hexagonal of La_2O_3 and cubic forms of CrO_2 phase are stabled. The size of nanoparticles is in the range from 20 to 60 nm as found with using x- powder method (Dercz et al., 2006; Zhu, 1998; Kurzweg et al., 1998; Betz et al., 1999; Kale et al., 2005; Cao et al., 2005) and shown in Figures 4 and 5. The amorphous structure is obtained at 300°C which can be used for gate dielectric of nano electronic devices. This amorphous structure has become to nano crystalline structure with heating the sample (Figure 2b, T = 500°C).

Conclusion

Lanthanum oxide (La_2O_3), also known as “lanthana” is usually supplied as an odourless white powder. It is

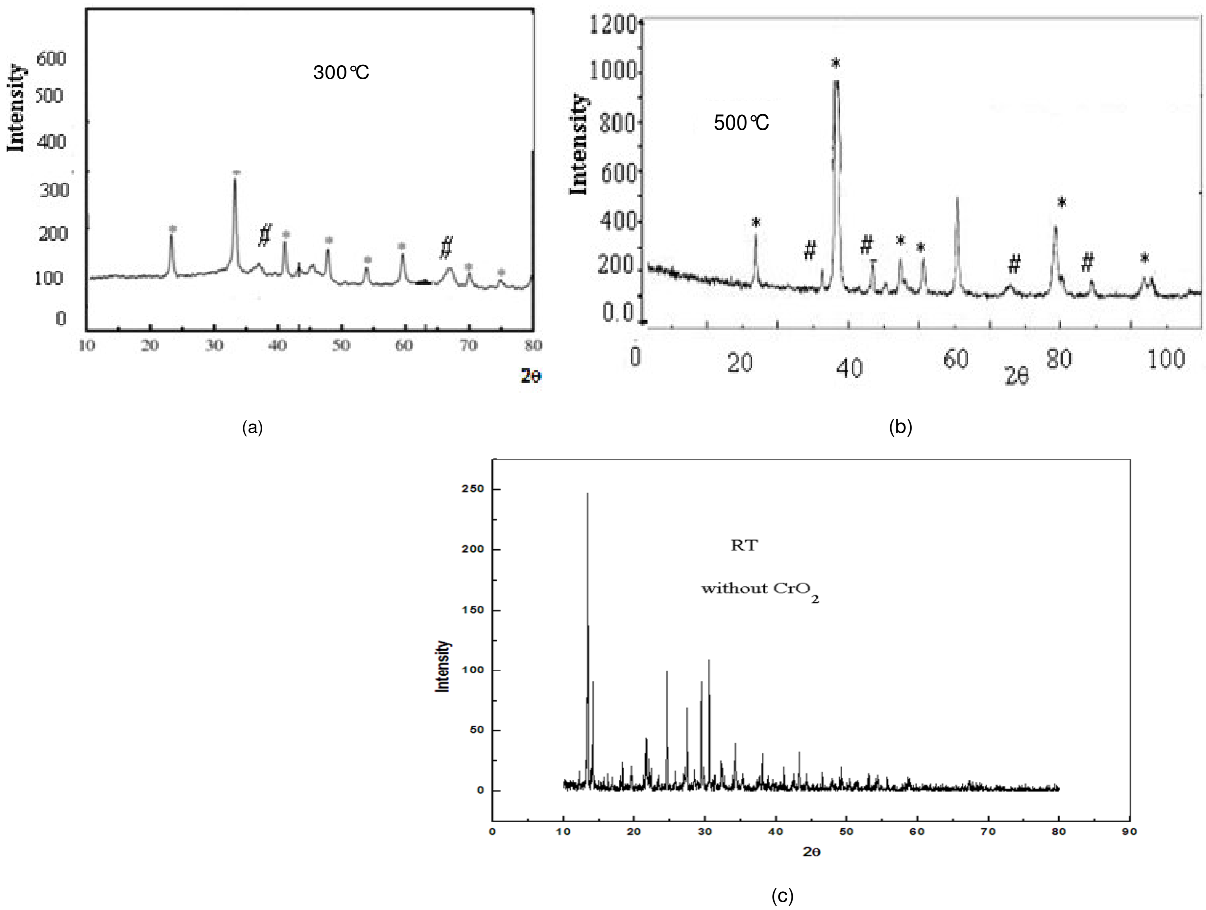

Figure 2. (a) The XRD pattern of nanoparticles at 300℃ without CrO_2. * Indicates the hexagonal crystal phase and # shows cubic crystal phase. (b) The XRD pattern of nanoparticles at 500℃ without CrO_2 and (c) The XRD pattern of nanoparticles at RT without CrO_2.

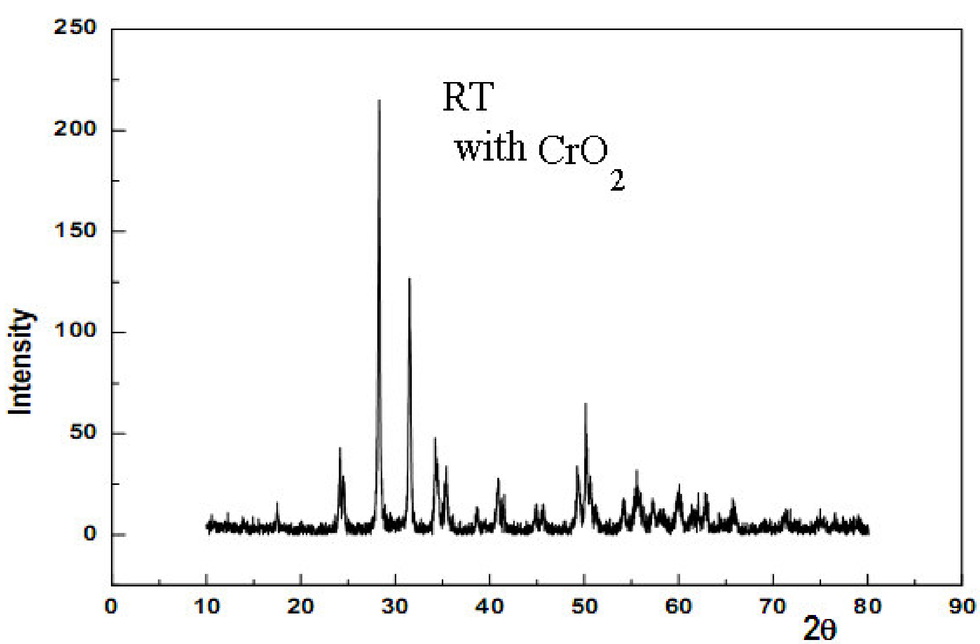

Figure 3. The XRD pattern of nanoparticles at RT with CrO_2 (50% wt La_2O_3 and 50% wt CrO_2).

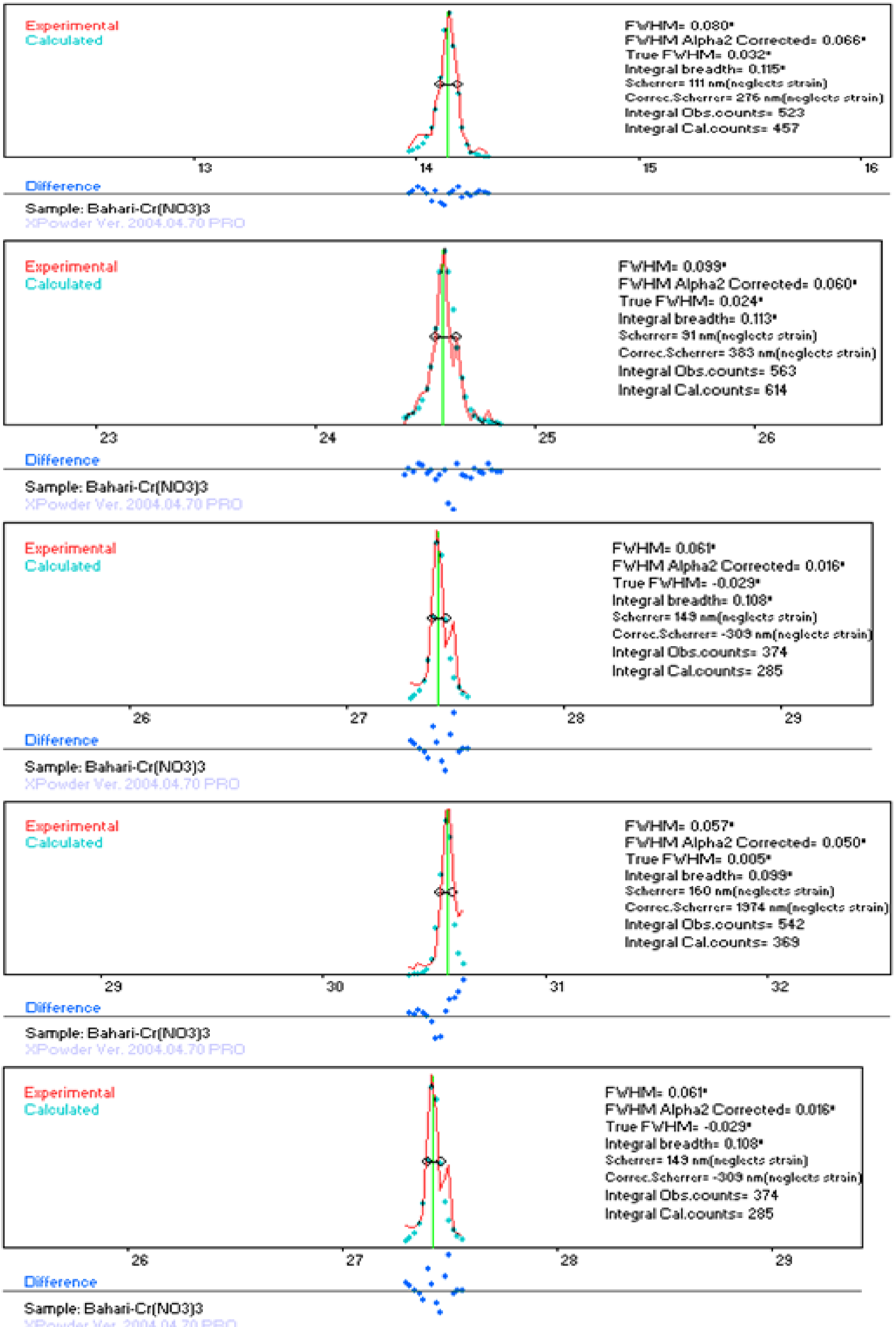

Figure 4. The size of nanoparticles correspond with Figure 2; and are determined using x- powder method.

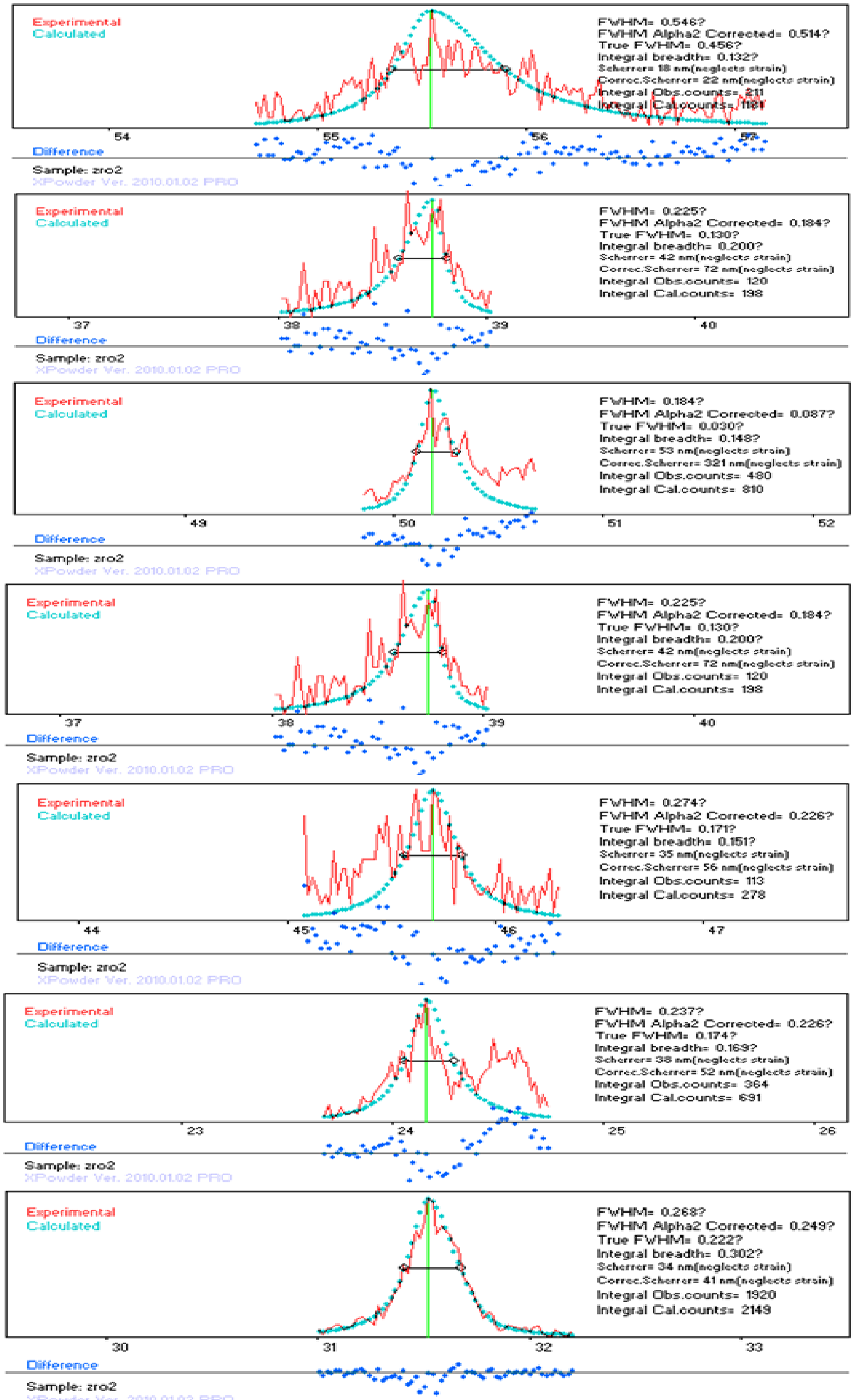

Figure 5. The size of nanoparticles correspond with Figure 3; and are determined using x- powder method.

slightly soluble in water and soluble in acids. La_2O_3 has been used to make optical glasses, to which this oxide confers increased density, refractive index and hardness. La_2O_3 in CrO_2 content have been synthesized at different temperatures. The fraction of the cubic La_2O_3 decreases at low temperature, whilst it increases at 500°C. It means that we could get the progressive phase transformation from metastable hexagonal La_2O_3 to stable cubic La_2O_3 during heating. In the XRD patterns, one can see the presence of cubic, hexagonal of La_2O_3 and cubic CrO_2 phases. In this spectrum, the intensity cubic "lanthania" is so small component which indicates this phase is interoperated into "lanthania" phases. The peak broadening at 500°C (respect to room temperature) indicated the bigger size of the crystallites in the growth direction.

The amorphous structure of sample (at 300°C) can be used as a good gate dielectric of nano electronic devices.

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