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Low Temperature Synthesis of ZrO_2 and CrO_2 by Sol – Gel Process

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Abstract: 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.
Moreover, ultra fine and pure ZrO_2/CrO_2 are also so important in ceramic technologies. We have demonstrated a series of experiments to synthesis ZrO_2 as well as CrO_2 at low temperature with using sol-gel method. The obtained results show that a ZrO_2/CrO_2 can be used as a gate for the future of nano electronic as well as nano particles in stability of Stainless Steel (SS) material of Ultra High Vacuum (UHV) chambers. These structures have been studied by using XRD technique.
Key words: Nano structures, Zirconium, Stainless steel and Sol-gel method.

Introduction

The gate SiO_2 dielectric thickness in current complementary metal oxide semiconductor (CMOS) transistors is less than 1 nm. Such a thin gate dielectric can not prevent leakage, tunneling currents and boron diffusion [1-7]. We have thus needed electrical permittivity insulators as the alternative gate dielectrics for future of CMIS (I: Insulator) devices. The ZrO_2/CrO_2 gate stacks with high electrical permittivity show an amorphous structure of low temperature which can fill this gap.

On the other hand, synthesizing the ultra–fine stacks has become of great interest in ceramic technologies [8-10], due to its excellent chemical properties [10-14] and independent ZrO_2 network within the CrO_2 network.

In this work, we have synthesized ZrO_2/CrO_2 which is suitable for CMIS. Its crystalline phase can be used for the potential applications of the ceramic – mesoporous structures as well. On the other hand, to grow an ultra thin oxide film we need a UHV chamber which can keep low pressure down to 10^{-14} Torr.

The current UHV chamber can not keep such a low pressure due to leakage and some unwanted bonds on the SS structures. We have thus tried to synthesize nano ZrO_2 /CrO_2 preduce in SS content to fabricate more stable SS - UHV chamber.

We have demonstrated to synthesis of tetragonal phase zirconia (t-ZrO_2) at room temprature by the sol-gel method, because of its excellent mechanical properties, such as fracture toughness, high strength and hardness [13-16].

However, ZrO_2 in SS content has still poor structure stability [17-23] due to its structural collapse during formation of the mesoporous phase and its phase transformation from tetragonal phase to monoclinic phase. For this reason, we synthesize CrO_2 nanoparticles in parallel to ZrO_2 nanoparticles in SS

structure and the obtained results indicate the potential applications of the present combination.

Experimental procedure and details

Zirconium dioxide was prepared by the hydrolysis and condensation of zirconium propoxide $Zr(OC_3H_7)_4$ used as precursor under acidic conditions. However, $[Zr(OC_3H_7)_4]$ is highly reactive and the hydrolysis is instantaneously leading to the uncontrolled precipitation of polydispersed powders as soon as water is added to the alcoxide solution. To circumvent this difficulty, the idea is to use esterification reaction, which counterbalances alcoxide solution hydrolysis. Thus the kinetic is conditioned and it is becoming possible to control hydrolysis rate. 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 following reactions.

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

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

Hydrolysis

$$Zr(OR)_3OR + H_2O \rightarrow Zr(OR)_3OH + ROH$$

Condensation

$$Zr(OR)_3OH + Zr(OR)_3OR \rightarrow (OR)_3Zr\text{-}O\text{-}Zr(OR)_3 + ROH$$

Or

$$Zr(OR)_3OH + Zr(OR)_3OH \rightarrow (OR)_3Zr\text{-}O\text{-}Zr(OR)_3 + H_2O$$

Where $OR = OC_3H_7$. The chemically controlled condensation of zirconium alkoxide leads to stable colloidal solutions of monodispersed zirconia nanoparticles.

The ZrO_2 sol was prepared from a zirconium alkoxid precursor [13-17], zirconium propoxide (Aldrich), acetic acid (sigma-aldrich) was used as a chelating agent to zirconium 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 zirconium propoxide and isopropanol at room temperature in the molar ratio 1 Zr: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-aldrich) and isopropanol. Acetic acid was added drop – wise to the stirred alkoxide solution until the molar ratio of acetic acid to Zr 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 above solution to produce a zirconia sol until the molar ratio of $Zr:CH_3COOH:HNO_3:\ H_2O:C_3H_7OH$ 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 ZrO_2 as well as SS (figures 2 and 3).

The properties of zirconia forms of higher symmetry are very often preferable to monoclinic one. CrO_2 is usually used as the stabilization component of higher symmetry zirconia [14-19].

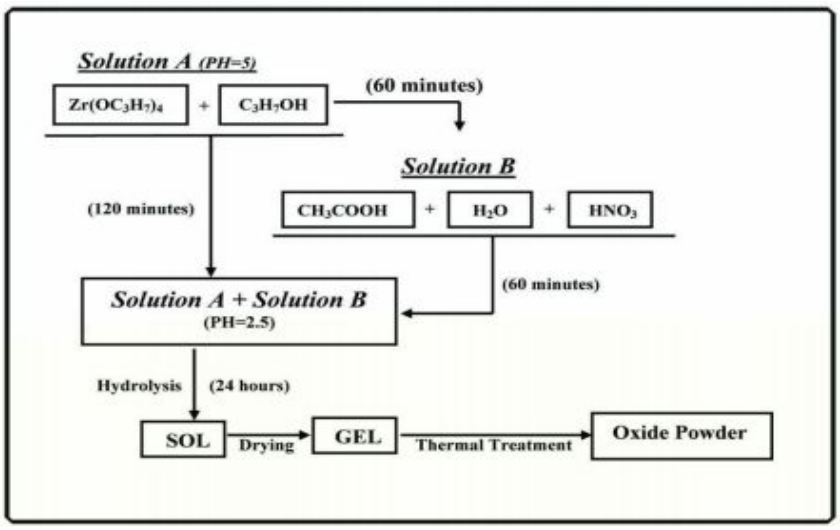

Figure 1 - Preparation steps of ZrO_2 powders. Similar procedure is for CrO_2.

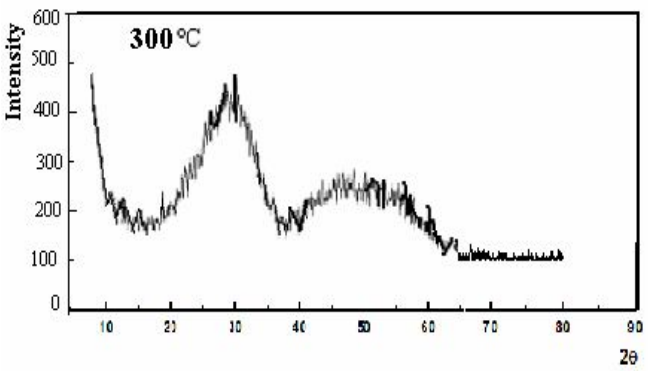

Figure 2 (a) - The XRD pattern of nanoparticles at 300^0C without CrO_2.

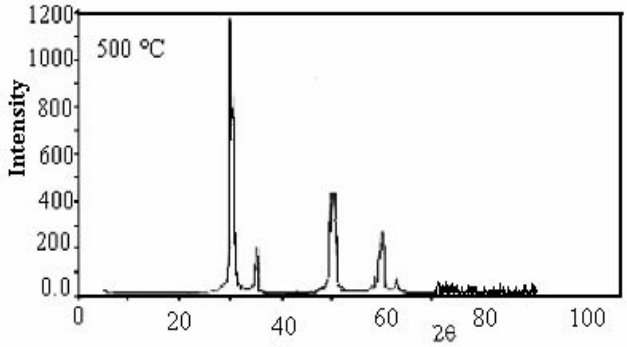

Figure 2 (b) - The XRD pattern of nanoparticles at 500^0C without CrO_2.

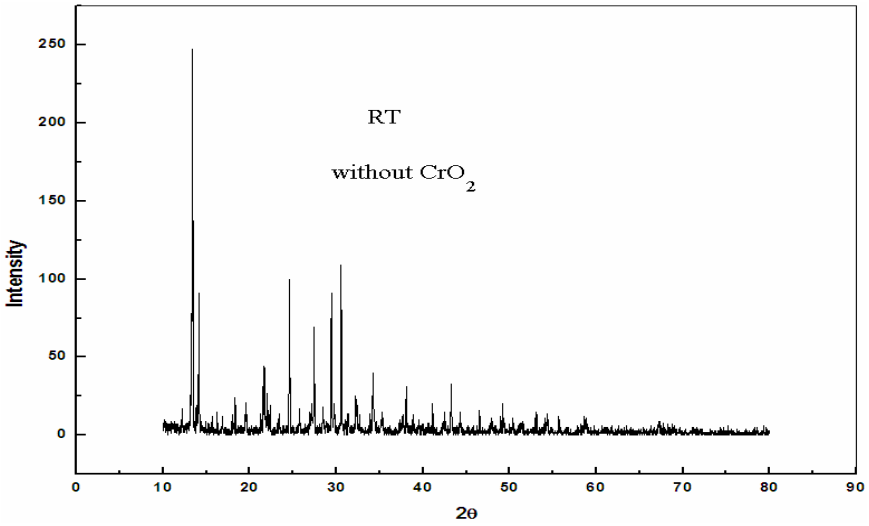

Figure 2 (c) - The XRD pattern of nanoparticles at RT without CrO_2.

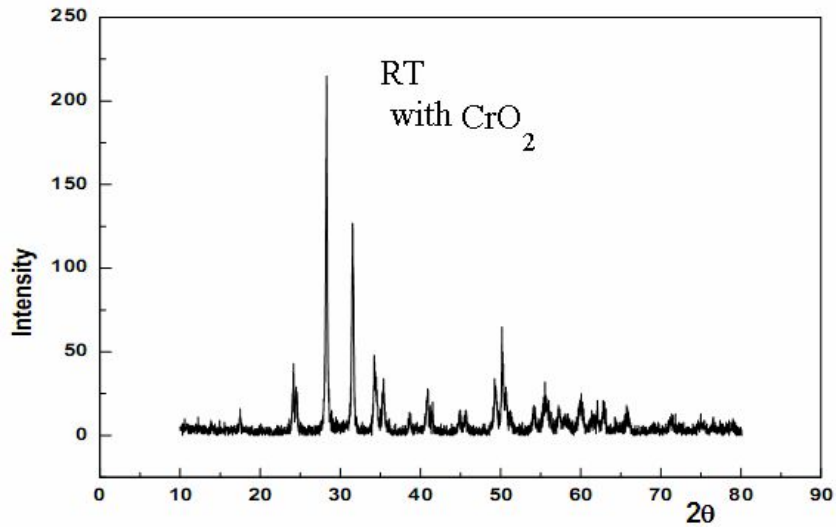

Figure 3 - The XRD pattern of nanoparticles at RT with CrO_2 (50% wt ZrO_2 and 50% wt CrO_2).

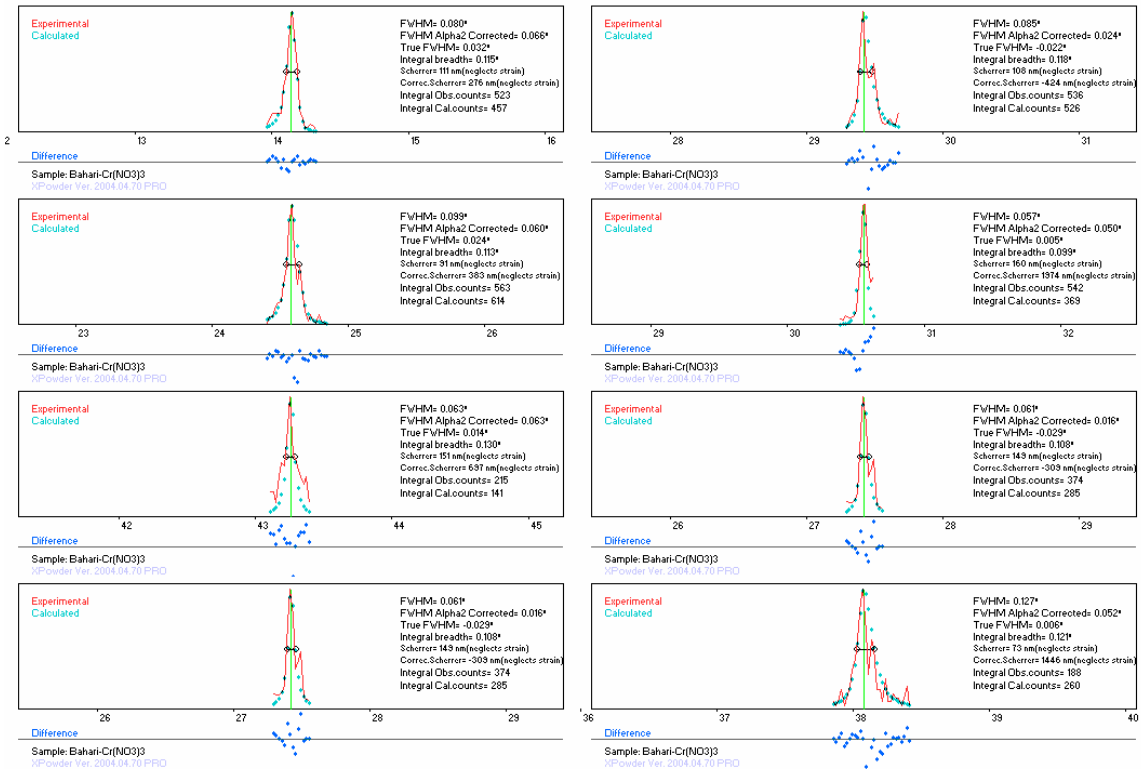

Figure 4 - The size of nanoparticles correspond with figure 2, are determined with using X- Powder method .

Figure 2 shows the XRD patterns of ZrO_2 without CrO_2. As one can see in figures 2 (c) peaks at 13°, 24°, 29-31 ° and 44 ° attributed to the (111), (200), (220) and (311) diffraction planes of the tetragonal zirconia, and some monoclinic zirconia peak at 50 ˚– 80 ˚. Figures 3 displays the XRD pattern ZrO_2 with CrO_2 (The presence of CrO_2 (50wt%) in ZrO_2 .). The new peaks in comparison to figure 2, attributed to CrO_2 phases. Phase beside of monoclinic, tetragonal of ZrO_2 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 [10-15] and shown in figures 4 and 5. The amorphous structure is obtained at 300^{0}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 (As an example see figure 2 b, T = 500^{0}C).

Conclusion

ZrO_2 with CrO_2 in SS have been synthesized at different temperatures. The fraction of the monoclinic ZrO_2 decreases at low temperature, whilst it increases at 500 ℃. It means that we could get the progressive phase transformation from metastable tetragonal ZrO_2 to stable monoclinic ZrO_2 during heating.

In the XRD patterns, one can see the presence of monoclinic, tetragonal of ZrO_2 and cubic CrO_2 phases. In this spectrum, the intensity cubic zirconia is so small component which indicates this phase is interoperated into zirconia phases. The peak broadening at 500 ℃ (respect to room temperature) indicated the bigger size of the crystallites in the growth direction. The amorphous structure of sample (at 300^{0}C) can be used as a good gate dielectric of nano electronic devices.

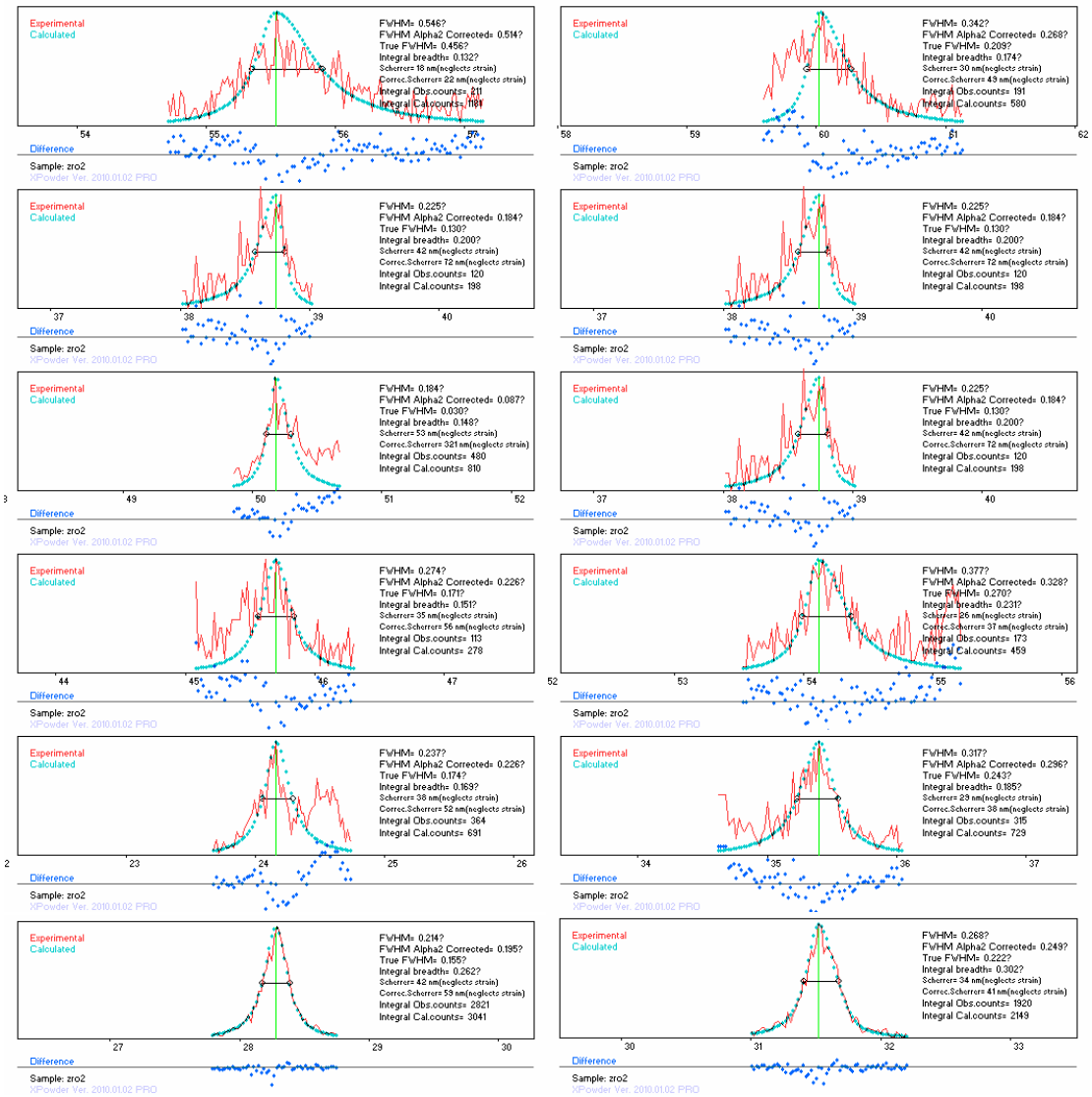

Figure 5 - The size of nanoparticles correspond with figure 3, are determined with using X- Powder method .

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