Growth Mode Study of $MgCl_2$ on Ti (0001) and SiO_2 Under Ultra High Vacuum by XPS

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Abstract - **The growth mode of MgCl2 on Ti (0001) and on SiO2 grown on Si (100) was investigated by X-ray Photoelectron Spectroscopy (XPS) under UHV conditions. Magnesium chloride grows on both Ti (0001) single crystal and SiO2 following the Frank-van der Merve, (FM) growth mode.**

Keywords- growth mode; MgCl2; Ti(0001); SiO2; UHV; XPS

I. INTRODUCTION

The deposition of $MgCl_2$ on a well characterized Ti surface and SiO_2 is of special interest in studies related to Ziegler-Natta catalysts which are used for the heterogeneous polymerization of olefins. In the so called third or fourth generations of Ti-based Ziegler-Natta catalysts, $TiCl_4$ is chemisorbed on "activated" magnesium chloride, a defective form of $MgCl_2$ with high Miller index planes exposed at the surface [1]. Many granular materials have been proposed as supports in modified Ziegler-Natta catalysts. Porous silicas, magnesium halides and their combination are the most important.

In order to extend the knowledge of such complex catalyst system at the atomic level, different scientific groups develop catalytic models compatible for study with surface sensitive techniques [2, 3]. The previous studies of our group, and in order to understand the nature of the catalytically active sites, were to simplify the model catalyst by depositing the catalyst components under UHV conditions. The first step in developing this ideal model catalyst, is the deposition of $MgCl_2$ on foils, single crystals [4] and on SiO_2/Si(100) well characterized substrates [5] which are studied by means of XPS.

The present work deals with the investigation of the growth mode of $MgCl_2$ on Ti (0001) and SiO_2 by X-ray Photoelectron Spectroscopy (XPS). For the purposes of the present study, $MgCl_2$ is applied on these supports by evaporation under UHV conditions.

II. EXPERIMENTAL

The experiments took place in the Surface Science Laboratory of Chemical Engineering Department of University of Patras. For the XPS measurements the non-monochromatic MgKα line was used with hν= 1253.6 eV. The hemispherical analyser (Leybold EA-11) was working at constant pass energy E_p=100 eV.

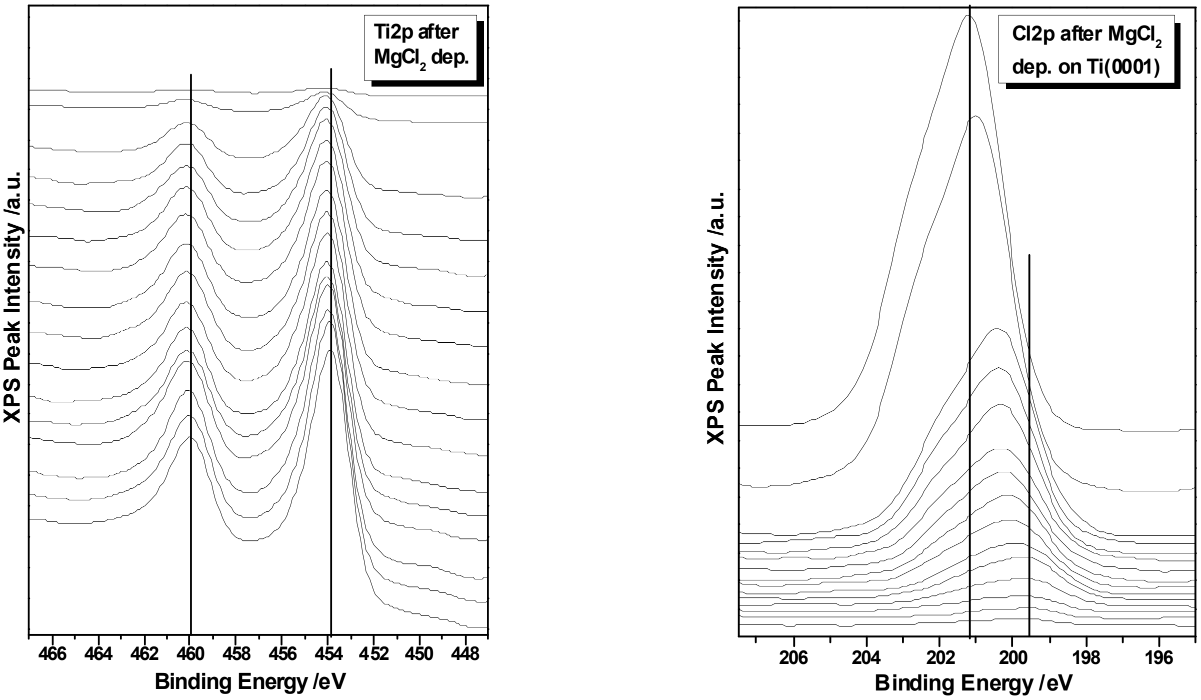
The first substrate used in this study, was a Ti (0001) disc (MaTecK), 10mm in diameter and 2mm thick, which was subjected to in-situ cleaning by repeated cycles of 1keV Ar^+ sputtering and annealing at 450 ^oC in order to remove C, S, and O and H contamination. Many cycles of this procedure produced a surface without impurities except for the small amount of hydrogen, the existence of which was eventually verified at the valence band spectra.

The second substrate was a p-type Si (100) single crystal. It was annealed in the atmosphere at 873 K for 60 min, in order to develop a thick SiO_2 layer on its surface. Before introduction in the ultra high vacuum (UHV) system the sample was chemically cleaned by immersion in a 2O2/NH4OH/H2O (1:1:5) solution at 323 K for 10 min in order to remove organic contaminants. The crystal was then transferred into the UHV system and annealed at 973 K for 15 min. This procedure leads to desorption of the largest percentage of hydroxyl species from the SiO_2 surface, leaving about 1–3 OH/nm^2 [6]. This is a common treatment of silica supports during the industrial preparation of Ziegler–Natta catalysts [7, 8].

Magnesium chloride was deposited under UHV conditions through a $MgCl_2$ evaporation source, described elsewhere [4]. All depositions were carried out at a source temperature of 795 K, while the substrate was held at room temperature. The Cl/Mg atomic ratio was found to be ~2 indicating that the deposit consists essentially of stoichiometric $MgCl_2$.

III. RESULTS AND DISCUSSION

After confirming the atomically clean Ti (0001) surface, a stepwise deposition procedure of $MgCl_2$ took place under UHV, at a constant source temperature of 795K, measuring the deposition time of each step in seconds. After each $MgCl_2$ deposition, two photoelectron peaks were recorded (Cl2p and Ti2p) as well as one (x-ray induced) Auger peak (MgKLL). Figure 1 shows the XPS spectra of Ti2p derived from the substrate and MgKLL, Cl2p originating from the deposit.



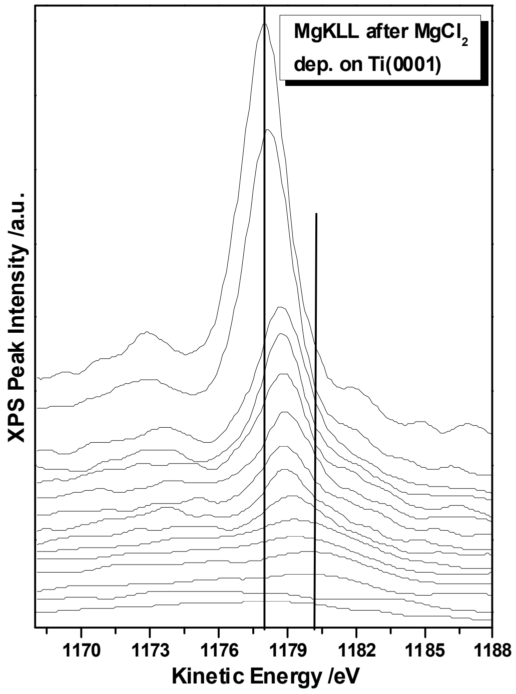


Fig. 1. XPS peak intensity of Ti2p, MgKLL and Cl2p spectrum after stepwise $MgCl_2$ deposition on Au foil at RT.

The Ti2p core level peak appears at binding energy (BE) 454.0eV and shifts by +0.3eV (BE) after $MgCl_2$ deposition indicating chemical interaction between the support and the deposit. The MgKLL auger photoelectron peak shifts -2.2eV to lower kinetic energy (KE) and the Cl2p core level peak shifts +1.5eV to higher BE after deposition of the maximum amount of $MgCl_2$ on the Ti single crystal. This is expected and has its origin to both interaction between the deposit and the substrate and to electrostatic charging of the deposited $MgCl_2$ layer, as $MgCl_2$ is an insulating material [4, 5, 9].

Figure 2 shows the intensity ratios of each one of the peaks originating from the deposit, divided by the intensity of the Ti2p of the substrate as a function of the deposition time. These graphs provide strong indication that $MgCl_2$ follows a layer by layer deposition on Ti(0001). The figure clearly shows a “break” of the lines slope after the completion of each monolayer pointing out a Frank-van der Merve, (FM) growth mode.

The same procedure of MgCl2 deposition took place also on SiO2/Si(100) substrate. Figure 3 shows the XPS spectra of Si2p derived from the substrate and MgKLL, Cl2p from the deposit.

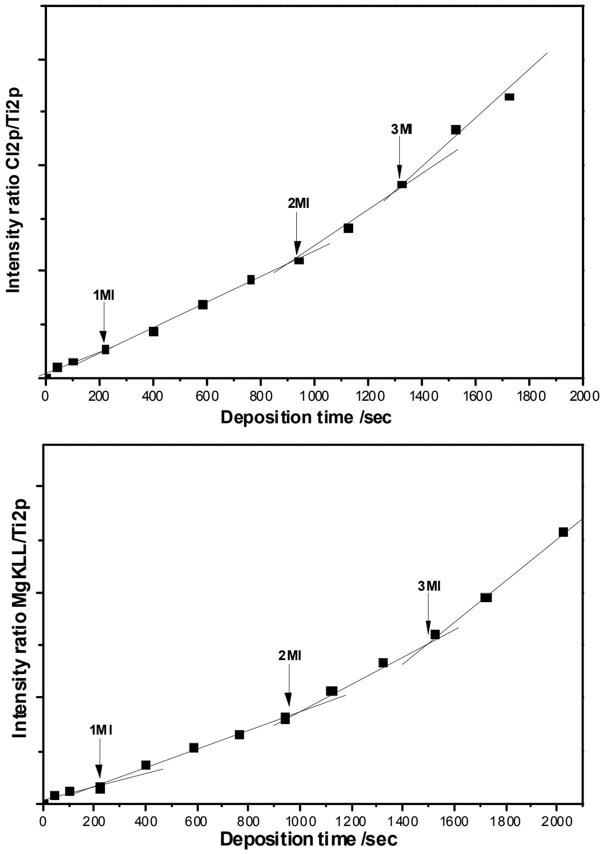
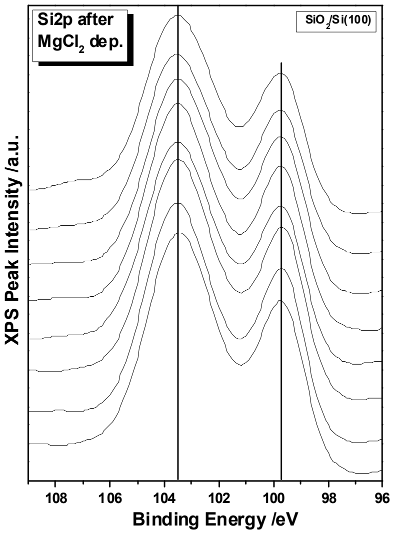
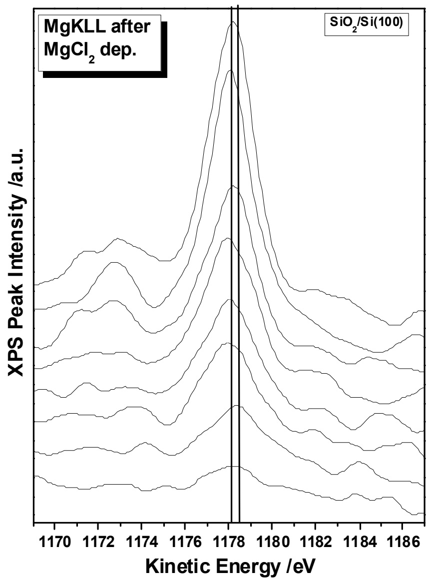


Fig. 2. Graphical representations of the ratios Cl2p/Ti2p and MgKLL/Ti2p as a function of the $MgCl_2$ deposition time.





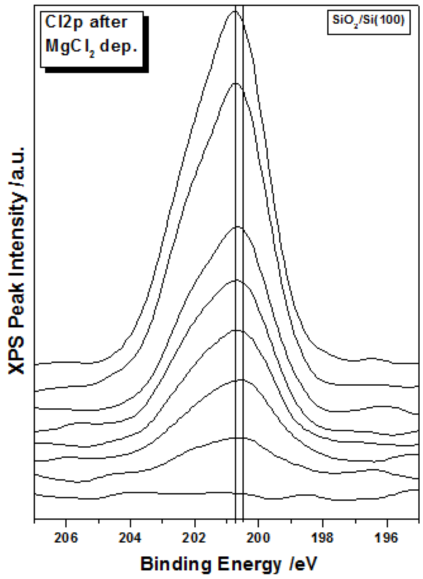


Fig. 3. XPS peak intensity of Si2p, MgKLL and Cl2p spectrum after stepwise $MgCl_2$ deposition on Si (111) 7x7 at RT.

The Si2p core level peak appears at BE= 99.5eV derived from the Si(100) and there is another component which appears at 103.5eV BE and derives from the oxide layer on top of the single crystal. The Si2p peak does not shift after $MgCl_2$ deposition indicating that in this case no chemical interaction between the support and the deposit takes place. The MgKLL auger peak shifts again by -0.3eV to lower KE and the Cl2p core level peak shifts +0.3eV to higher BE after deposition of the maximum amount of $MgCl_2$ on SiO_2. These shifts appear due to electrostatic charging of the deposited $MgCl_2$ layer.

Figure 4 shows the intensity ratios of each one of the peaks originating from the deposit, divided by the intensity of the

Si2p of the substrate as a function of the deposition time. These graphs provide also in this case strong indication that $MgCl_2$ follows a layer by layer deposition on Ti(0001). The figure clearly shows a "break" of the lines slope after the completion of each monolayer pointing out a Frank-van der Merve, (FM) growth mode.

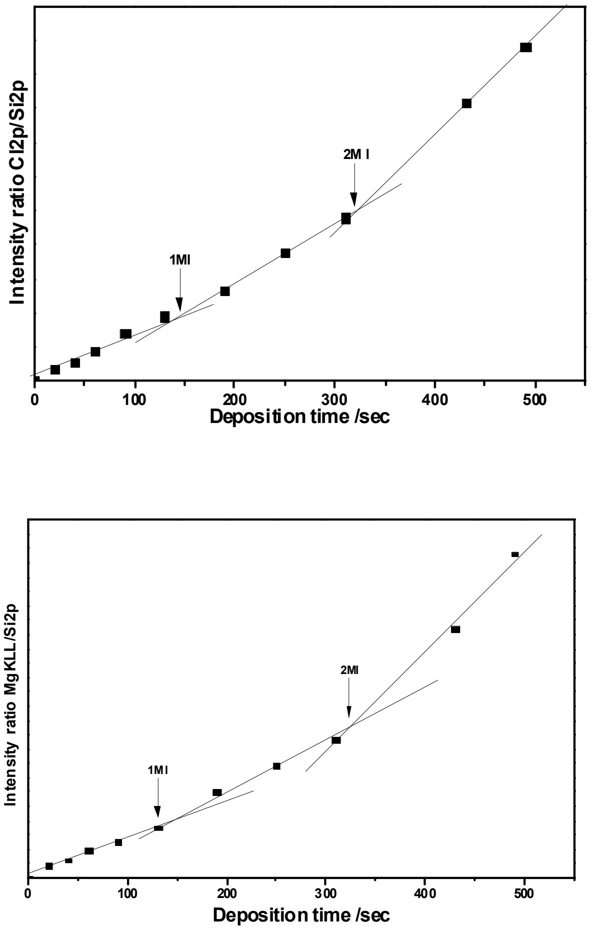


Fig. 4. Graphical representations of the ratios Cl2p/Si2p and MgKLL/Si2p as a function of the $MgCl_2$ deposition time.

IV. CONCLUSIONS

The $MgCl_2$ was deposited on the atomically clean surface of the Ti (0001) single crystal. The deposition took place via a layer by layer growth mode. Chemical interaction between the deposit and the substrate was observed while the energy shifts of the $MgCl_2$ photoelectron peaks occurred due to this interaction and due to electrostatic charging. Energy shifts were also observed after deposition of $MgCl_2$ on SiO_2/Si (100) due to the insulating nature of the deposit. The growth of $MgCl_2$ on the SiO_2 surface follows also the Frank-van der Merve, (FM) mode.

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Stavros Karakalos was born in Athens in 1979. He received a B.S. in Physics from the University of Ioannina in 2003, an MSc in Material Science and Technology and a Ph.D. in Chemical Engineering – Surface Science in 2009. He worked as a Post Doctoral Researcher at the Foundation for Research and Technology, Institute of Chemical Engineering and High Temperature Chemical Processes in Patras and as a part time teacher in the Technological Educational Institute of Patras, Greece. Presently he is a Postdoctoral Employee in University of California Riverside. His research interests include the use of a large variety of surface analysis and characterization techniques in order to determine the structure, composition and electronic properties of the outermost atomic layers of solid materials exposed to ultra-high-vacuum or controlled gaseous atmospheres and correlate them with the material behavior in various processes. His main research interests include Surface Science aspects of Heterogeneous Catalysis.