Growth mode study of MgCl₂ on Au foil and Si (111) 7x7, under Ultra High Vacuum by XPS

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Abstract - **The growth mode of MgCl2 on Au foil and Si (111) 7x7 reconstructed surface under UHV conditions, was investigated by X-ray Photoelectron Spectroscopy (XPS). Magnesium chloride grows with the Frank-van der Merve, (FM) growth mode on the Au foil. On Si surface there is evidence for the layer by layer growth of MgCl2 but leaving uncovered silicon areas at the first steps of deposition due to the Si (111)7x7 surface roughness.**

Keywords- growth mode; MgCl2; Au foil; Si(111)7x7; UHV; XPS

I.   INTRODUCTION

Magnesium Chloride is one of the most important magnesium compounds as far as industrial applications are concerned. In catalysis, $MgCl_2$ is used in Ziegler-Natta (ZN) catalyst preparation [1]. Supported on $MgCl_2$ or on mixed $MgCl_2/SiO_2$ supports, Ziegler-Natta catalysts are used for the industrial olefin polymerization and the production of polymers, such as isotactic polypropylene or high density and linear low-density polyethylene. ZN catalysts are the best candidates for the low pressure production of linear low-density polyethylene and ethylene co-polymers from the gas phase, with improved optical properties in the film form. Magni and Somorjai [2] studied model Ti-based Ziegler-Natta catalysts prepared by $MgCl_2$ sublimation under ultra high vacuum (UHV) conditions onto a gold foil.

Surface sensitive spectroscopies comprise the most effective means of investigating the growth mode of $MgCl_2$ on various substrates providing significant information of the surface composition and structure. Nevertheless, the study of different $MgCl_2$ interfaces at a molecular level is a particularly difficult task due to the sensitivity of magnesium chloride to oxygen and humidity. Furthermore, the poor conductivity of $MgCl_2$ makes surface analysis rather complicated.

In the preset work, the growth mode of $MgCl_2$ on Au foil and Si (111) 7x7 is investigated 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 $MgK\alpha$ line was used with $h\nu= 1253.6$ eV. The hemispherical analyser (Leybold EA-11) was working at constant pass energy $E_p=100$ eV.

The Au foil was subjected to Ar^+ sputtering in order to gain an atomically clean surface. The Si(111) single crystal substrate, 10mm x 10mm (Mateck), which could be heated up to 1200K, was subjected to cycles of Ar^+ sputtering and annealing at 1200K in order to remove C and O contamination and cooled back to RT with a constant rate of -1K/sec, in order to obtain the 7x7 reconstructed surface which was confirmed by a Low Energy Electron Diffraction (LEED) image (not shown here).

$MgCl_2$ was deposited in Ultra High Vacuum (UHV) through a magnesium chloride evaporation source, described elsewhere [3]. All depositions were carried out at a source temperature of 795K, 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 Au surface, a stepwise deposition procedure of $MgCl_2$ took place under UHV, at the constant source temperature of 795K, measuring the deposition time of each step in seconds. After each $MgCl_2$ deposition, three photoelectron peaks were recorded. Figure 1 shows the XPS spectra of Au4f derived from the substrate and MgKLL, Cl2p coming from the deposit.

The Au4f core level peak appears at 84.1eV binding energy (BE) and it is not shifted after $MgCl_2$ deposition indicating no chemical interaction between the support and the deposit. The MgKLL auger photoelectron peak shifts 1.9eV to lower kinetic energy (KE) and the Cl2p core level peak shifts 0.63eV to higher BE after deposition of the maximum amount of $MgCl_2$ on Au foil.
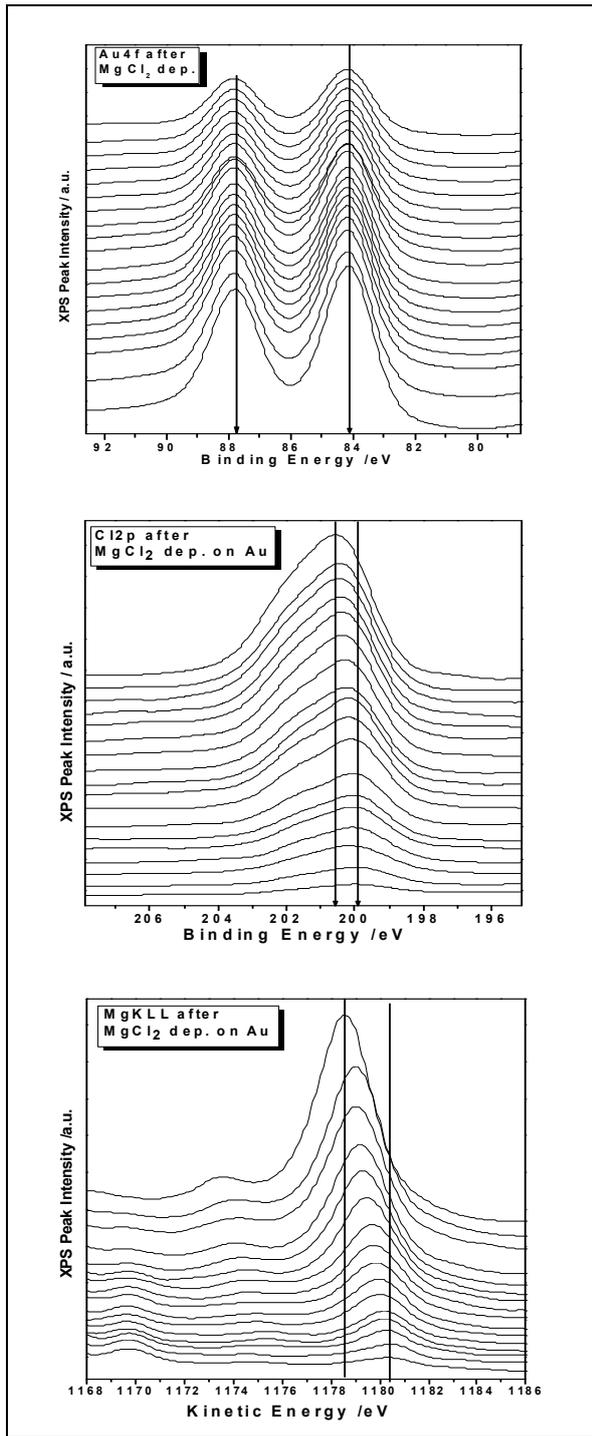
Figure 1.   XPS peak intensity of Au4f, MgKLL and Cl2p spectrum after stepwise MgCl₂ deposition on Au foil at RT.

This is an expected observation [3],[4] due to electrostatic charging of the deposited MgCl₂ layer, as MgCl₂ is an insulating material.
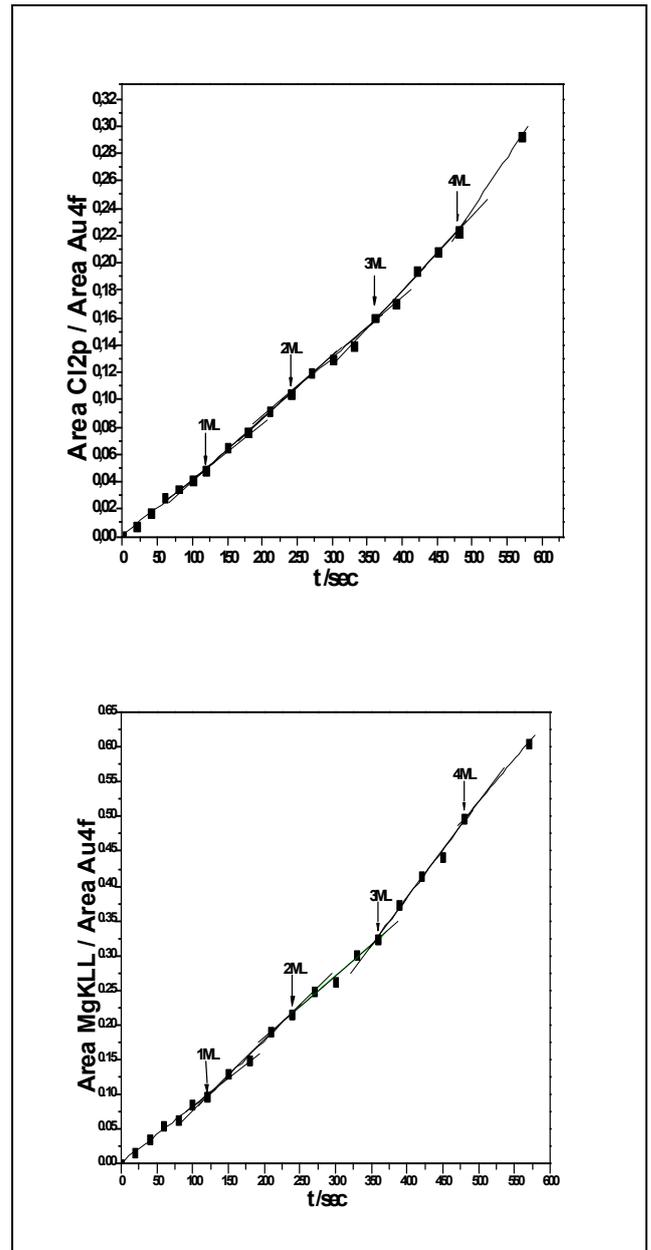
Figure 2.   Graphical representations of the ratios Cl2p/Au4f and MgKLL/Au4f as a function of the MgCl₂ deposition time.

Figure 2 shows the ratio of the intensity of each of the two XPS peak of the deposit, divided with the intensity of the Au4f of the substrate as a function of the deposition time of each step. It is observed that there is strong indication that MgCl₂ follows a layer by layer deposition. The figure shows that the completion of each layer is obvious and this is a Frank-van der Merve, (FM) growth mode.

The same procedure of MgCl₂ deposition took place also on Si (111) 7x7 substrate. Figure 3 shows the XPS spectra of Si2p derived from the substrate and MgKLL, Cl2p coming from the deposit. The Si2p core level peak appears at 99.5eV BE and it is not shifted after MgCl₂ deposition indicating that also in this

case no chemical interaction between the support and the deposit takes place. The MgKLL auger photoelectron peak shifts again by 1.9eV to KE and the Cl2p core level peak shifts 2.1eV to higher BE after deposition of the maximum amount of $MgCl_2$ on Si single crystal. These shifts are observed due to electrostatic charging of the deposited $MgCl_2$ layer.

Figure 4 (a) shows the ratio of the intensity of Cl2p photoelectron peak of the deposit, divided with the intensity of the Si2p of the substrate as a function of the deposition time of each step. In this case there are no obvious changes in the slope of the line, indicating that there is no layer by layer growth of the deposit. Although, fig.4 (b) shows an almost exponential increase of MgKLL intensity as a function of deposition time which is characteristic of layer by layer growth of the deposit through the law of Beer. This observation could be explained by taking into account that the reconstructed Si (111)7x7 surface is a very rough surface

Figure 3.   XPS peak intensity of Si2p, MgKLL and Cl2p spectrum after stepwise $MgCl_2$ deposition on Si (111) 7x7 at RT.
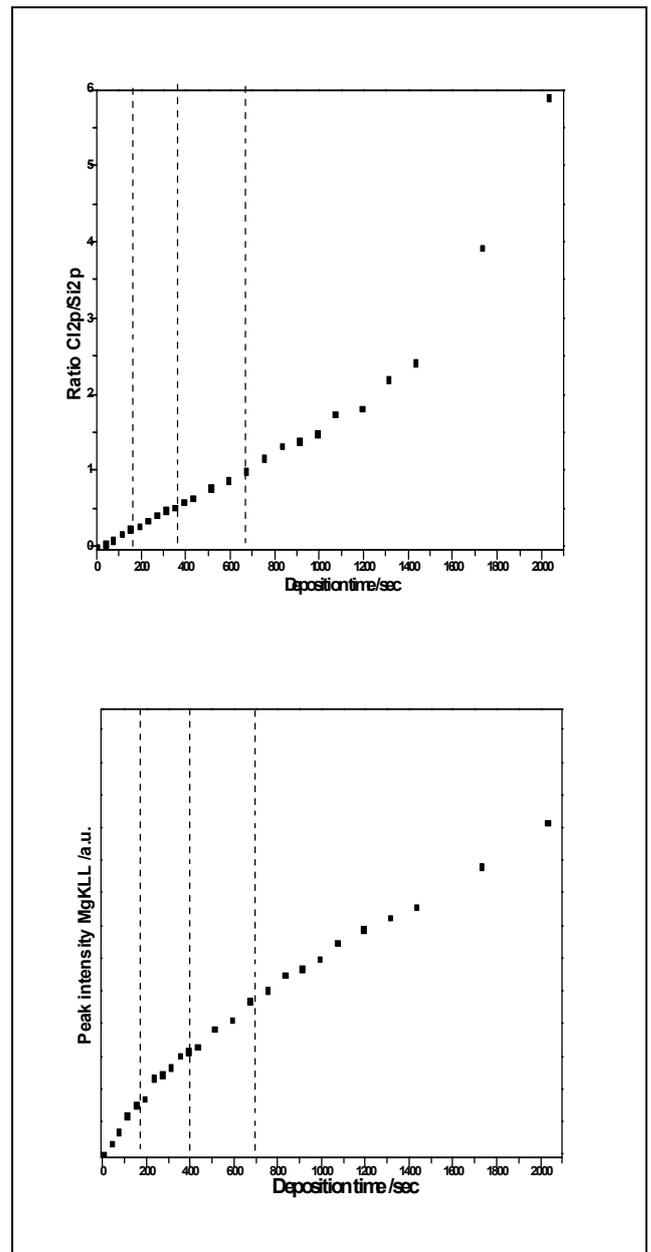
Figure 4.   Graphical representations of the ratios Cl2p/Si2p and MgKLL/Si2p as a function of the $MgCl_2$ deposition time.

Figure 5 shows that the well characterized Si (111)7x7 surface consists of a large number of Si atoms which extrude outside the 1x1 level. This might cause different behavior of the ratio Cl2p/Si2p as a function of deposition time, even for layer by layer growth of the $MgCl_2$. During the first steps of deposition the layer of $MgCl_2$ may leave uncovered the Si atoms which extrude outside the surface. Moreover, this surface roughness would not affect the MgKLL intensity as a function of deposition time, which should appear as exponential increase for a layer by layer growth following the law of Beer.
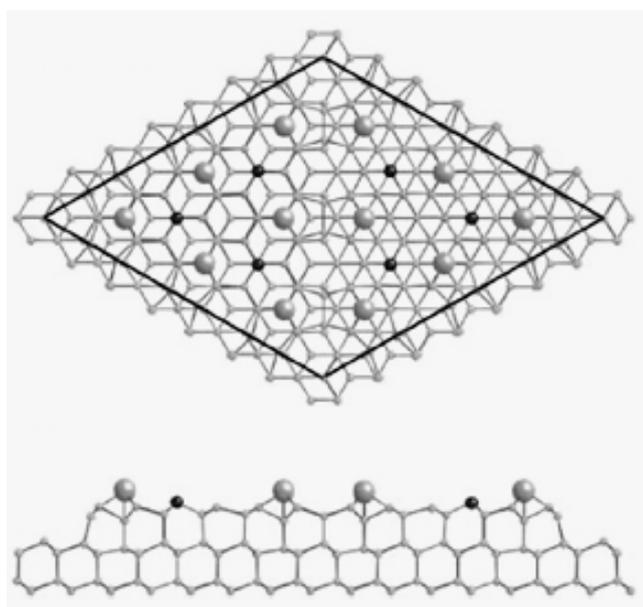
Figure 5.   Representation of the Si (111) 7x7 reconstructed surface.

IV.   CONCLUSIONS

The $MgCl_2$ deposited on the atomically clean Au foil surface resulted in a layer by layer growth. No interaction between the deposit and the substrate was observed and the energy shifts of the $MgCl_2$ photoelectron peaks were obvious due to electrostatic charging. Similar energy shifts were observed after deposition of $MgCl_2$ on Si(111)7x7 due to the insulating nature of the deposit. The growth mode of $MgCl_2$ the Si surface indicates the Frank-van der Merve, (FM) growth mode, but leaving uncovered areas of silicon at the first steps of the deposition.

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Stavros Karakalos was born in Athens in 1979. He received B.S. in Physics from the University of Ioannina in 2003, MSc in Material Science and Technology and Ph.D. in Chemical Engineering – Surface Science in 2009. Presently he is Post Doctoral Researcher at the Foundation for Research and Technology, Institute of Chemical Engineering and High Temperature Chemical Processes in Patras, Greece. 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.