Valence and Core Electron Spectra of Mg in MgO in Evoporated Thin Films

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(Z. Naturforsch. **30 a,** 1485—1490 [1975]; received June 28, 1975)

X-ray photoelectron spectra (XPS) are obtained for Mg in MgO using high quality (purity 99.999%) Mg films prepared and oxidized under pressures of $10^{-6} \sim 10^{-8}$ torr and measured on an ESCA-36 spectrometer at a pressure of 10^{-8} torr. AlKα line source was used for excitation, and the minimum of Au valence band at 5.0 eV was chosen for calibration.

With increased oxidation the valence band shifts about 1.0 eV towards the Fermi level, but with extreme contamination it disappears completely. Accurate measurements of binding energies have been made of Mg in pure Mg, and Mg in MgO. The average shift resulting from oxidation is 1.1 eV for Mg(2s) and 1.5 eV for Mg(2p) core levels. It is also observed that the contamination effect due to oxygen decreases with increasing film thickness. The present results are compared with the previous results, and a new interpretation is offered by postulating the formation of two kinds of oxides, stoichiometric and chemisorbed layers in Mg on oxidation.

I. Introduction

X-ray photoelectron spectroscopy (XPS) is one of the most important techniques for studying the electronic band structures of solids [1], amorphous solids [2], liquids [3] and gases [4]. We will use this technique to study the surface properties of Mg in MgO. The band structure of bulk Mg is well known, and has been rather extensively studied by various methods [5–7]. We [8] have previously reported our study of the Auger electron spectroscopy (AES) on Mg thin films with oxidation. We have noted in that study quite substantial line shifts for some of the KLL Auger transitions accompanied by partial or complete disappearance of some transitions with oxidation. We concluded from these results that there are two kinds of oxides formed on the surface or near the surface, stoichiometric and chemisorbed layers. We would now like to report our additional experimental results of the oxidized Mg films obtained by measuring the valence and core electron spectra of Mg via the XPS technique.

Presently, several reports [9–20] are available on the XPS study of Mg along with AES and UPS (ultraviolet photoelectron spectroscopy) studies. While Gesell et al. [9] studied the optical and photoelectron properties by the UPS method in the photon energy range $2 \sim 10$ eV, Wagner and Biloen [10] followed the effect of oxidation on Mg thin films by the AES method. The latter group observed some chemical shifts in the AES and XPS lines with oxidation. Feuerbacher and Fitton [11] investigated the collective electron oscillations in the thin films of Zn, Cd and Mg. For Mg, in particular, they noted that the first plasmon peak occurred at 10.21 eV with the corresponding electron lifetime of about 1.09×10^{-15} sec. A number of interesting papers have been published by Tejeda et al. [12] on Mg alloys, especially on Mg_2Sn. These workers have emphasized a sizable difference in the binding energies in the XPS and AES spectra with various alloying constituents, such as, Si, Ge and Sn. There is also some evidence of the chemical effect on the XPS spectra of Mg; this has been demonstrated with the single crystal study of $Mg(OH)_2$ for different crystallographic directions [13]. In this work a marked anisotropy in the valence band spectra was found. Most recently, Ley et al. [14] have studied the many body effects in the XPS and AES spectra of pure Mg and compared their results with the corresponding theoretical results.

Of all these studies, however, there are two very recent papers on Mg, one by Ley et al. [14], and the other by Fuggle et al. [19] which are worth mentioning. Ley et al. [14] have studied the many body effect on the XPS and AES of ultrapure Mg films deposited and measured in pressures of 3×10^{-9} and 6×10^{-11} torr respectively. This study reveals somewhat higher energies for the KLL Auger transitions. These energy values and the observed core level energies of the

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Mg spectra were interpreted, perhaps for the first time, by introducing the possibility of many body effects in the form of extraatomic relaxation process. On the other hand, Fuggle et al.[19] have measured both the XPS and AES of Mg, and Mg in compounds of MgO, Mg_2Cu, Mg_3Au and Mg_3Bi_2. In this study these authors[19] claimed to have achieved a better resolution and accuracy than some of the earlier[10, 12, 16] works in that they observed a number of (five) plasmon loss peaks in the Mg(2 s) core spectra and six in the KLL Auger spectra. Interestingly, Ley et al.[14] found a number of plasmon loss peaks in their Mg(2 p) core spectra. Fuggle et al.[19] further noted that, in most part, the KLL Auger transitions in pure Mg always occurred at higher transition energies than those of Mg in the compounds.

The main purpose, however, in this work is to detect and characterize the changes in the valence and core electron spectra of Mg with oxidation by analyzing the photoelectron energy spectrum obtained with different oxidized samples. Since Mg is highly reactive to oxygen, and since a systematic study of Mg with oxidation is not known, a study as mentioned above, will be quite important and worthwhile. We will, in particular, be interested in the characterization of different types of oxide layers which might form during oxidation.

II. Experimental

High quality Mg of purity 99.999% obtained from Ventron Corporation was used. Several films of various thicknesses ranging from 200 to 25,000 Å were prepared onto ultraclean microscope glass slides in the pressure range of $10^{-6} \sim 10^{-8}$ torr.

The rate of deposition of the films and temperature of the substrates were accurately monitored. The former was achieved by using a Sloan Omni IIA thickness monitoring system, which consists of the "control unit" and the "sensor head". A quartz crystal with a resonant frequency of 5 Hz is used into the oscillator head. The frequency of the oscillator decreases when a deposit of the evaporant builds up with time indicating the correct thickness on a precalibrated scale. The thickness control system operates by comparing the changing frequency of the crystal to a tunable reference signal. The temperature of the substrate can be controlled by passing a desired current through a set of heating coils via an automatic thermocouple on-off switch. In the present experiment only room temperature deposition was made at zero input current through the coils, and the temperature was maintained constant for all the films. The ambient atmosphere was dehumidified dry air of the laboratory and no extra effort was made to preheat the remaining air in the vacuum chamber. The rate of deposition was about 20 Å/sec.

The identification of the films was done on the basis of the "gettering phenomena", which we shall explain later in this paper, in the decreasing order of oxidation of the first few monolayers as viewed from the top of the films. That is to say thicker films (1 – 4 only) have less available O_2 to form oxide layers on the top surfaces. Film 5 was especially prepared in very high vacuum to reproduce as far as practicable pure Mg results.

Five films were studied which were identified as:
Film 1, 2 and 3 with thicknesses 200, 1000 and 5000 Å respectively are prepared at a pressure of $10^{-6} \sim 10^{-7}$ torr at room temperature.
Film 4 with thickness 25,000 Å is prepared at a pressure of 10^{-6} torr at room temperature.
Film 5 with thickness about 200 Å is prepared at a pressure of about 10^{-8} at room temperature.

The XPS measurements were made on an ESCA-36 photoelectron spectrometer. The AlKα (1486.6 eV) line was used for the excitation. The pressure in the spectrometer chamber was maintained at about 10^{-8} eV throughout the experiment.

To record the exact value of the binding energy, the stability of the spectrometer was checked periodically by identifying the O(1 s) and C(1 s) lines. The calibration of the spectrometer was further checked against the valence band spectra of pure Au-film deposited directly onto a glass slide inside the spectrometer vacuum chamber. Figure 1 shows the valence band spectra of pure Au, which was used for final calibration.

The Fermi energy of our samples was normalized to zero, and the binding energy E_b was obtained from the incident photon energy $h\nu$:

$$h\nu = W_{sp} + E_b + E_k , \tag{1}$$

where W_{sp} is the work function of the spectrometer and E_k the kinetic energy of the electrons. For our spectrometer with AlKα radiation the above equation reduces to, in eV,

$$1486.6 = 4.5 + E_b + E_k . \tag{2}$$

Substitution of the photon energy and the spectrometer work function (4.5 eV for the spectrometer used in this investigation) in the binding energy equation gives the XPS binding energies:

$$E_b = 1486.6 - 4.5 - E_K . \tag{3}$$

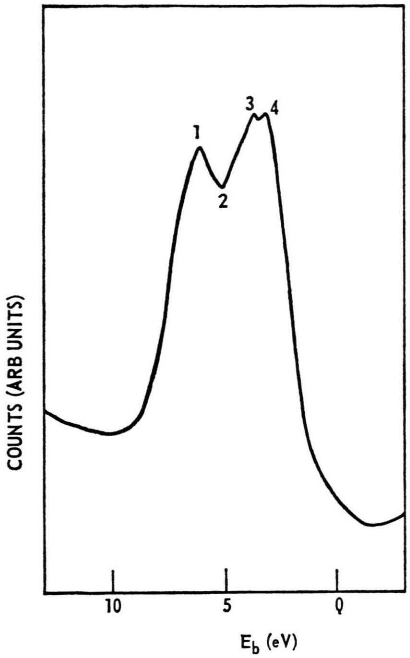

Fig. 1. The valence band spectra of pure Au. The minimum at 5.0 eV was used for consistency and recalibration each time.

Fig. 2. The valence and core electron spectra of Mg in MgO for film 1 and film 5. Film 1: solid line; film 5: broken line. →

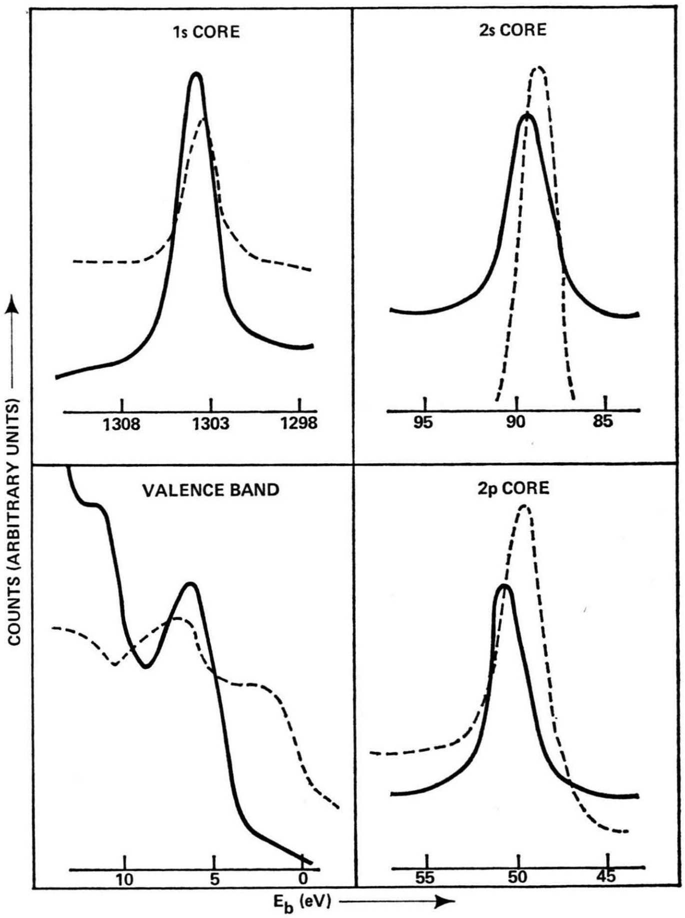

Table 1. Binding Energies of Mg Core Level Peaks in Mg Films in eV.

Film No.	n l			
	1 s	2 s	2 p	3 s
1	1304.0	89.5	51.0	—
2	1304.3	89.4	50.9	—
3	1304.3	89.7	50.9	—
4	1304.1	89.6	50.8	1.0
1−4 Avg.	1304.2	89.6	50.9	1.0
5	1303.6	88.5	49.4	2.0

While the results for individual films are summarized in Table I, we show the spectra for two extreme cases, film 1 and film 5 in Figure 2. The films showing distinctly the valence band Mg(3 s) peak are films 4 and 5. The valence band peak seems to shift to a higher binding energy with a decrease in surface oxidation. The core levels show an overall shift to higher binding energies with an increase surface oxidation. Finally, two oxygen species were observed, one at 530.5 eV for film 5 and the other at about 532.0 eV for films 1 − 4.

III. Results and Discussions

The O(2 p) electrons with peak position at 7 eV dominates, in most parts, the valence band structures in films 1, 2 and 3. In films 4 and 5, however, the valence band Mg(3 s) peak is visible indicating a shift of about 1.0 eV due to oxidation. The shift of Mg(3 s) peak of film 4 to a lower binding energy indicates a greater sharing of electrons with O_2, i.e. the formation of a stronger oxide bond. The Mg(3 s) peak position at 2.0 eV in film 5 agrees well with that obtained by Ley et al.[14] for the case where there is one core electron hole state available. In our study no such information could be extracted from any shifts in the O(2 p) valence electrons, because of the presence of contaminating carbon valence band C(2 p) in the region of 7 eV.

In the present study we are purposefully dealing with Mg in two phases, Mg in Mg and Mg in MgO. This MgO is expected to be the stoichiometric compound formed during evaporation of the films in an oxygen shrouded atomsphere in the pressure range $10^{-6} \sim 10^{-8}$ torr. The core level spectra should indicate the influence of this oxidation. A surface that consists of two phases such as in films 2, 3 and 4, will have two sets of core levels. The peaks will be resolved if the peak sizes are comparable and the separation is large enough (on the order of 0.5 eV). However, in this study one phase is dominant over the other, for example MgO in films 2, 3 and 4, but Mg in film 5. Table II shows the average binding energy values of the core levels along with the previous results[4, 14, 19]. A comparison of the core peak positions obtained from film 5, which represents our pure Mg, with those obtained by Ley et al.[14] shows excellent agreement. The 0.6 eV discrepancy of the Mg(1 s) level between our result and that of Ley et al.[14] is perhaps due to some oxidation still present in our film 5. It has been suggested[21] that the electrons escaping from 1 s levels have lower kinetic energy than those from other levels and consequently are more sensitive to the changes in the surface environment than the others.

Table 2. Comparison of Binding Energies of Mg in eV.

n l	Present Work Mg	 MgO	Ref. 4 MgO	Ref. 14 Mg	Ref. 19 Mg	 MgO
1 s	1303.6	1304.2	1305.0	1303.0	1303.4	1305.3
2 s	88.5	89.6	89.0	88.6	89.0	90.4
2 p	49.4	50.9	52.0	49.4	49.9	51.6

In our previous study[8] of AES of Mg in MgO, we have detected the evidence of two kinds of oxides, one is usual stoichiometric MgO as mentioned above, and the other is the chemisorbed MgO formed after deposition, may be during measurement/sample transfer/sample positioning, etc. It is quite likely that the above films have some of both kinds of MgO. We could further conclude the occurrence of both kinds of oxides in our films by observing the binding energy of O(1 s) level, which ranged between 531.8 and 530.8 eV, although the positions of valence band minimum of Au and maximum of C(1 s) level remained unshifted at 5.0 and 284.8 eV respectively throughout the experiment. It should, however, be noted that the probability of seeing the spectra from stoichiometric MgO is much greater than that of chemisorbed MgO in films 2, 3 and 4 than in film 5. The spectra of film 5, in all likelihood, could be from chemisorbed MgO.

Although none of the films had comparable concentrations of both phases present so that dual core peaks could be observed, it was still possible to obtain a good estimate of the core level shifts of metallic Mg to stoichiometric MgO. A comparison of the peak positions of film 5 (hcp pure metal structure) with those of film 1 (fcc MgO-type structure) reveals that core shifts of about 1.0 eV for the Mg(2 s) and 1.6 eV for the (Mg(2 p) occur. No estimate of the Mg(1 s) level shift is presented, because the sensitivity of this level to surface conditions is rather high. Other investigators[21] have studied metal oxide systems and observed that the difference between the metal core positions in the metal oxide in the crystalline form and the metal oxide in chemisorbed form is small, on the order of 0.2−0.3 eV. O_2 in these systems, however, shows somewhat larger differences, on the order of 1.0 eV. The metal oxide in the crystal form has of course the higher binding energy. Therefore, in the absence of any experimental error in the binding energy value, error due to nonuniform surface of crystalline MgO can be estimated to roughly 0.3 eV. Wagner and Biloen[10] obtained a double phase Mg-MgO surface with a comparable abundance of each and was able to measure the shift for the Mg(2 s) level directly. Our estimation of the Mg(2 s) peak shift at about 0.9 eV is in excellent agreement with their measurement of 1.0±0.2 eV. The Mg(2 p) peak shift had not previously been reported.

The O(1 s) binding energy in chemisorbed MgO in film 5 has a value of 530.5 eV compared to the O(1 s) values for films 1−4, which are about 532 eV. The latter value is higher than what we expected, because the binding energy of O_2 in MgO crystal should have a lower energy than that in chemisorbed MgO, which predicts a stronger bond. It is suggested that the O_2 peaks observed in films 1−4 are due to an adsorbed layer of some kind of O_2 species on their surfaces, which cover the smaller crystalline O_2 peaks.

As already discussed in previous sections, the energy difference between the core levels of an element in a compound is characteristic of the bond in that particular compound. Thus, the energy difference between the Mg(2 s) and Mg(2 p) peaks should decrease with oxidation. This energy difference in film 5 (the pure metallic film) is 39.1 eV, and in film 1−4 (crystalline MgO) is 38.7 eV. The latter energy difference agrees well with the energy difference of 38.8 eV noted in crystalline MgO in a recent investigation[22]. A similar study by Fuggle et al.[19] indicates a shift of 39.1 eV, which agrees with our film 5.

IV. Conclusions

In conclusion, we find that the oxidation has some pronounced and distinct effect on the XPS of Mg. In particular, we note that the valence band shifts to a lower binding energy by about 1.0 eV, when a stoichiometric bond is formed. Similarly the Mg(2 s) and Mg(2 p) core spectra respectively shift by about 1.0 and 1.6 eV, when a stoichiometric bond is formed. Apparently, the Mg(1 s) core is more sensitive to the surface modifications than other core spectra, as evidenced by the 0.6 eV discrepancy between our result and the previous results in less contaminated environment. This comes from the fact that the escaping Mg(1 s) electrons have much lower kinetic energies than those from the other electrons. The O(1 s) electrons in the chemisorbed MgO species were found to have binding energy equal to 530.5 eV. Then the energy difference between the Mg(2 s) and Mg(2 p) electrons becomes 38.7 eV in the stoichiometric state, and 39.1 eV in the pure metallic state. These differences may be considered as the characteristic of these two types of Mg in different states. Finally, in our study the core spectra in film 5 are the characteristic of pure hcp Mg with little chemisorbed MgO, whereas those in films 1 – 4 are the characteristic of the stoichiometric fcc MgO. We demonstrate this picture by drawing an energy level diagram in Figure 3 of pure Mg and its two oxides. A similar conclusion, as mentioned before, was also reached[8] from a study of the AES results.

Fuggle et al.[19] have reported a binding energy of 531.0 eV for the O(1 s) line in their most recent work of MgO. However, unlike our work, they carried out their oxidation in an atmosphere of dry O_2 or degassed water vapor. A difference of about 0.5 eV between the present work and Fuggle et al.[19] could come from the difference in the O_2 atmosphere used in the two respective investigations. In the wet atmosphere there is a possibility of formation of $Mg(OH)_2$ along with MgO. For this reason, O(1 s) line in $Mg(OH)_2$ and in MgO will differ with regard to their binding energies. Study of kinetics of formations of such oxides and hydroxides O(1 s) line belonging to either of the compounds have been also carried out by Fuggle et alias[19].

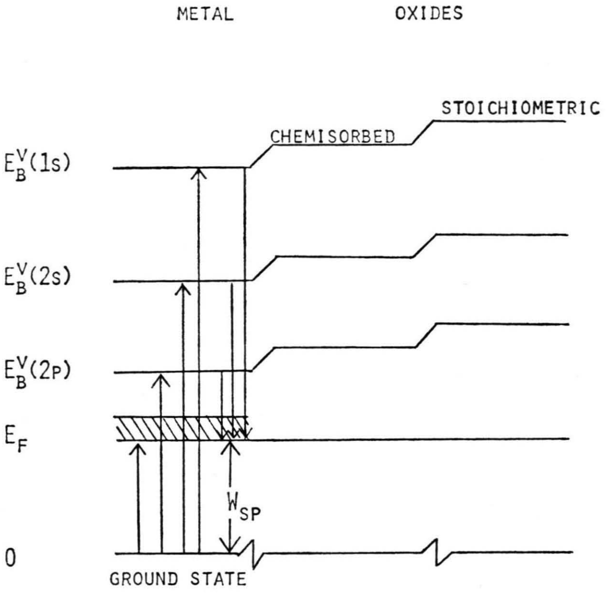

Fig. 3. Energy level diagrams of Mg and its oxides, showing the: (A) photoelectron emission and (B) x-ray emission involving various core levels.

Acknowledgements

Grants from the Petroleum Research Fund, administered by the American Chemical Society, and Research Corporation are gratefully acknowledged for partial support of this work.

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