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X-Ray Photoelectron Study of New Mixed Oxynitrides 'AlGaPON'

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Abstract

The galloaluminophosphate oxynitrides 'AlGaPON' are phosphates in which oxygen is substituted by nitrogen, by temperature-programmed activation under ammonia. By varying the time of nitridation at 750°C, four oxynitrides with variable nitrogen contents were obtained. They were studied by X-ray photoelectron spectroscopy and compared to the oxide precursor. Care was taken to demonstrate that with the Mg anode Ga Auger and photoelectric peak superposition did not prevent a quantitative approach of the 'AlGaPON' surface composition. This study shows that the oxygen/nitrogen substitution occurs preferentially around phosphorous and gallium atoms rather than around aluminium atoms. The good correlation between surface and bulk nitrogen content suggests a homogeneous nitridation. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

The substitution of oxygen by nitrogen in oxynitrides leads to compounds with specific properties and applications, as compared to oxides. For instance, the preparation of aluminophosphate oxynitrides 'AlPON' by temperature-programmed activation under ammonia stream of amorphous oxide precursors leads to a new family of catalysts with very promising acido-basic properties.[1–4] Indeed, substitution of oxygen by nitrogen increases the 'AlPON' surface basicity, which allows their use as basic catalysts in the Knoevenagel-type condensation.

Since the synthesis of oxynitrides by ammonolysis of reactive oxides requires the control of numerous synthesis parameters, very few systematic studies have been conducted on those compounds as compared to oxides.[5] Thus the development of new oxynitride-type materials first requires the perfecting of synthesis and characterization techniques.

In this study in particular, we present the synthesis of a new family of galloaluminophosphate oxynitrides, the 'AlGaPON', synthesized as amorphous products with high surface area by nitridation of an $Al_{0.5}Ga_{0.5}PO_4$ oxide. A series of four oxynitrides of general formula $Al_{0.5}Ga_{0.5}PO_{(8-3y)/2}N_y$, with variable nitrogen contents: 5, 11, 16 and 23 wt%N, were obtained by varying only the time of nitridation at 750°C. Those oxynitrides and the oxide precursor were studied by X-ray photoelectron spectroscopy. Care was taken to demonstrate that with the Mg anode Ga Auger and photoelectric peak superposition did not prevent a quantitative approach of the 'AlGaPON' surface composition.

2 Experimental

2.1 Preparation of the $Al_{0.5}Ga_{0.5}PO_4$ galloaluminophosphate precursor

The $Al_{0.5}Ga_{0.5}PO_4$ galloaluminophosphate precursor was synthesized as X-ray amorphous product using a sol-gel process developed by Kearby[7] for $AlPO_4$ and adapted for '(Ga,Al)PO'. The starting products were $GaCl_3$, $AlCl_3$ and H_3PO_4 2 M. The solution containing gallium, aluminium and phosphorous with Ga/Al and P/(Ga + Al) ratios equal to 1 was cooled at 0°C with a dry ice–alcohol bath, then propylene oxide was slowly added under vigorous stirring. In fact, a large excess of propylene oxide was added with respect to the theoretical amount of 3 moles of propylene oxide per mole of the desired product, until the progressively increasing pH reached a value of 2·5. The transformation into a gel occurred after standing for some hours at room temperature. The gel was then repetitively washed with isopropanol without any loss of gallium, aluminium or phosphorous and progressively dried up to 110°C.

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Finally, the resulting powder was sifted ($< 100\,\mu m$) and calcined for 3 h at 650°C.

2.2 Nitridation

Oxynitrides $Al_{0\cdot5}Ga_{0\cdot5}PO_{(8-3y)/2}N_y$ were synthesized by nitridation in flowing pure ammonia of the oxide precursor placed in the isothermal region of a tubular furnace. This treatment led to 'AlGaPON' oxynitrides according to the following reaction:

$$Al_{0\cdot5}Ga_{0\cdot5}PO_4 + yNH_3 \xrightarrow{750^\circ C} Al_{0\cdot5}Ga_{0\cdot5}PO_{(8-3y)/2}N_y + 3y/2H_2O$$

'AlGaPON' with various nitrogen contents were prepared by varying the time of nitridation at 750°C. At the end of the nitridation, ammonia was replaced by nitrogen before furnace cooling.

The specific surface area of the samples was measured by the adsorption of nitrogen at liquid nitrogen temperature by single point BET method ($p/p_o = 0\cdot3$) after outgass 20 min at 250°C, using a Micromeritics Flowsorb II 2300 equipment.

2.3 Nitrogen analysis

The total amount of nitrogen (bulk nitrogen of nitride-type and hydrogenated NH_x surface species) was determined by Grekov titration[6]: the ammonia produced by reaction at 400°C of the nitride ions N^{3-} with melted potassium hydroxide is dissolved in water and titrated with sulphuric acid.

2.4 X-ray photoelectron spectroscopy analysis

One characteristic of XPS gallium spectra is the presence of numerous Auger peaks, in the region of kinetic energies varying from 830 to 1254 eV.[8] To determine whether Ga Auger and photoelectric peak superposition prevented a quantitative approach of the 'AlGaPON' surface composition, we had to combine data obtained with both Al (SSI SSX—100/206—monochromatized Al) and Mg (VG ESCA 3MkII—non-monochromatized Mg).

The VG ESCA-3MkII is an old-generation spectrometer, using a Mg non-monochromatized X-ray anode source, a hemispherical analyser and a channel electron multiplier as a detection system. Details concerning this kind of spectrometer have been given previously.[9,10] The Mg non-monochromatized X-ray anode source (1253·6 eV) was operated at 14 kV and 20 mA. The routine pressure of the analysis chamber was $< 10^{-8}$ Torr.

The SSI X-probe (SSX-100/206) of Fisons is a new-generation spectrometer consisting of a monochromatized microfocus Al X-ray source, an electron collection lens, a hemispherical analyser and a microchannel plate as detector. Details concerning this kind of spectrometer have been given previously.[11]

The Al monochromatized X-ray anode source (1486·6 eV) was operated at 10 kV. The residual pressure during the analysis remained between 1 and 5×10^{-9} Torr. A low energy flood gun (6 eV) with an Ni grid placed 3 mm above the samples was used to compensate for charging during measurements.

Binding energies were calculated with respect to the C–(C,H) component of the C_{1s} adventitious carbon fixed at 284·8 eV. The peaks recorded were C_{1S}, O_{1s}, N_{1s}, Al_{2p}, P_{2p}, P_{2s} and Ga_{3d}. The spectra were decomposed with the least-squares fitting routine with a Gaussian/Lorentzian ratio of 85/15 and after subtraction of a nonlinear baseline. The atomic ratios were calculated from relative intensifies corrected by:

- the elemental sensitivity factors provided by the manufacturer for the spectra taken with the SSI apparatus. In the calculation of those factors the Scofield's photoionization cross-section were used;[12]
- the Weng sensitivity factors for the spectra taken with the VG apparatus.[13]

3 Results and Discussion

Characteristics of both oxide and oxynitride powders as well as experimental conditions of activation are given in Table 1. This table evidences that the bulk nitrogen content of the samples increases with the time of nitridation. This evolution is illustrated in Fig. 1. As for the 'AlPON'[1] and 'ZrPON'[14] systems, the total nitrogen content tends towards a maximum.

The nitrided samples are characterized by lower specific surface areas (145–170 m²/g) than those of the precursor (240 m²/g). However, the decrease of surface area mostly takes place at the beginning of the nitridation; then the surface area is not significantly affected by the time of nitridation.

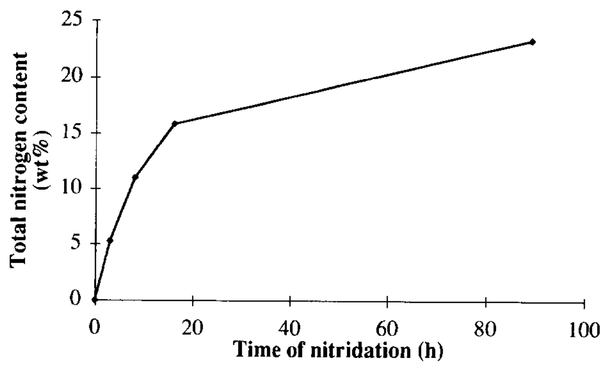

Fig. 1. Evolution of the total nitrogen content with the time of nitridation.

Table 1. Characteristics of the oxide and oxynitride powders studied

Sample	*Composition*	*Nitridation*		N_{total} *(wt%)*	S_{BET} *(m²/g)*
		Time (h)	*Temp. (°C)*		
AG9	$Al_{0\cdot5}Ga_{0\cdot5}PO_4$	—	—	—	240
AG9N2	$Al_{0\cdot5}Ga_{0\cdot5}PO_{3\cdot22}N_{0\cdot52}$	3	750	5·3	150
AG9N4	$Al_{0\cdot5}Ga_{0\cdot5}PO_{2\cdot43}N_{1\cdot04}$	8	750	11·0	160
AG9N5	$Al_{0\cdot5}Ga_{0\cdot5}PO_{1\cdot81}N_{1\cdot46}$	16	750	15·9	145
AG9N6	$Al_{0\cdot5}Ga_{0\cdot5}PO_{0\cdot94}N_{2\cdot04}$	89	750	23·3	170

XPS spectra contain two types of peaks: photoelectric peaks and Auger peaks. For the first, we speak of binding energies, for the second, the concept of kinetic energies is more adequate. Indeed, the kinetic energy of an Auger electron is independent of the X-ray source energy. By modifying the source energy, one can modify relative positions of Auger and photoelectric peaks.

It has been evidenced that using the Mg anode both the P_{2p} and P_{2s} photoelectric peaks were superposed to Ga Auger peaks. In addition, as the Ga Auger peak superposed to the P_{2s} photoelectric peak ($L_3M_{45}M_{45}$; KE: 1065 eV) is referenced as a major Auger peak,[8] it was decided to work with the P_{2p} photoelectric peak. Furthermore, with the Al anode, the N_{1s} photoelectric peak is superposed to a Ga Auger peak.

Therefore it was decided not to decompose the Ga Auger and photoelectric peaks but to compare atomic ratios evaluated with both anodes to determine whether peak superposition significantly affected the quantitative results.

The surface atomic ratios evaluated with both Al and Mg anodes are presented in Table 2. Al_{2p}/Ga_{3d} atomic ratios should be exactly the same when evaluated either with the Mg or the Al anode. However, they are not: this can be attributed to the different procedures used to evaluate the sensitivity factors on VG and SSI apparatus.[12,15]

From this table, we conclude that the Al_{2p}/N_{1s} atomic ratio evaluated with the Al anode is different to the one obtained with the Mg anode, especially for samples with the lowest nitrogen contents: it is significantly affected by the N_{1s}–Ga Auger peak superposition and cannot be used for quantitative measurements. However, Al_{2p}/P_{2p} atomic ratios evaluated with both Al and Mg anodes are very similar, suggesting that the P_{2p}–Ga Auger peak superposition with the Mg anode does not prevent a quantitative approach of the surface atomic composition. The atomic surface percentages evaluated with the Mg anode and the global atomic percentages evaluated by chemical analysis are presented in Table 3: surface and bulk atomic percentages are very similar.

As can be seen in Fig. 2, there is a good correlation between both the bulk nitrogen content detection method and the X-ray photoelectron spectroscopy quantification method, suggesting a homogeneous nitridation. A slight surface contamination of the oxyde precursor AG9 by ammonium species (BE: 401 eV) is observed.

Table 2. Comparison of the surface atomic ratios evaluated with both Al and Mg anode

	Al anode				*Mg anode*			
Sample	Al_{2p}/O_{1s}	Al_{2p}/N_{1s}	Al_{2p}/P_{2p}	Al_{2p}/Ga_{3a}	Al_{2p}/O_{1s}	Al_{2p}/N_{1s}	Al_{2p}/P_{2p}	Al_{2p}/Ga_{3d}
AG9	0·11	—	0·49	1·11	0·13	—	0·54	1·03
AG9N2	0·15	0·39	0·49	1·13	0·15	0·97	0·54	1·13
AG9N4	0·16	0·36	0·47	1·03	0·18	0·58	0·55	1·11
AG9N5	0·15	0·38	0·64	1·15	0·21	0·37	0·52	1·02
AG9N6	0·30	0·16	0·41	0·82	0·35	0·19	0·41	0·72

Table 3. Comparison of the surface atomic compositions evaluated with the Mg anode and the global atomic compositions evaluated by chemical analysis

	Surface atomic composition (%) XPS-Mg anode					*Bulk atomic composition (%) chemical analysis*				
Sample	*N*	*O*	*Ga*	*Al*	*P*	*N*	*O*	*Ga*	*Al*	*P*
AG9	1·04	65·80	8·39	8·65	16·12	0·00	66·67	8·33	8·33	16·17
AG9N2	9·11	57·70	7·82	8·87	16·50	9·06	56·10	8·71	8·71	17·42
AG9N4	15·64	50·91	8·13	9·02	16·30	19·01	44·42	9·14	9·14	18·28
AG9N5	23·47	42·29	8·58	8·80	16·86	27·70	34·35	9·49	9·49	18·98
AG9N6	40·55	21·94	10·80	7·74	18·96	40·96	18·88	10·04	10·04	20·08

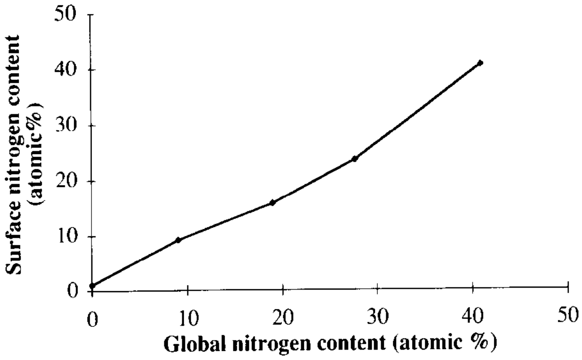

Fig. 2. Evolution of the surface nitrogen content with the global nitrogen content.

Table 4. Binding energies measured with the SSI apparatus

Sample	*$O_{1s}BE$ (eV)*	*$N_{1s}BE$ (eV)*	*$P_{2p}BE$ (eV)*		*$Al_{2p}BE$ (eV)*	*$Ga_{3d}BE$ (eV)*
			$2p_{1/2}$	*$2p_{3/2}$*		
AG9	532·3	—	134·3	135·3	75·4	21·4
AG9N2	532·1	398·3	134·0	135·0	75·3	21·0
AG9N4	532·1	398·1	133·8	134·8	75·2	20·7
AG9N5	531·8	397·8	133·3	134·3	74·8	20·4
AG9N6	531·8	397·8	133·1	134·1	74·5	20·4

The apparent defect in surface Al atoms for the sample with the highest nitrogen content (AG9N6) has not yet been explained.

Table 4 presents the binding energies evaluated with the SSI X-probe of the five elements present in 'AlGaPON' solids.

The general decreasing trend of the P_{2p} (Fig. 3), Ga_{3d} (Fig. 4) and Al_{2p} (Fig. 5) binding energies with the nitrogen content is explained by the better nucleophilic character of nitrogen compared to oxygen, which reduces the positive charge around those atoms.[4]

The P_{2p} and Ga_{3d} binding energies decrease progressively with the nitrogen content. For Al_{2p}, however, this decrease becomes significant (>0·2 eV) only for nitrogen content superior to 10 wt%, suggesting that oxygen substitution by nitrogen occurs preferentially around gallium and phosphorous atoms. For a nitrogen content superior to 10 wt%, oxygen bound to aluminium is substituted by nitrogen.

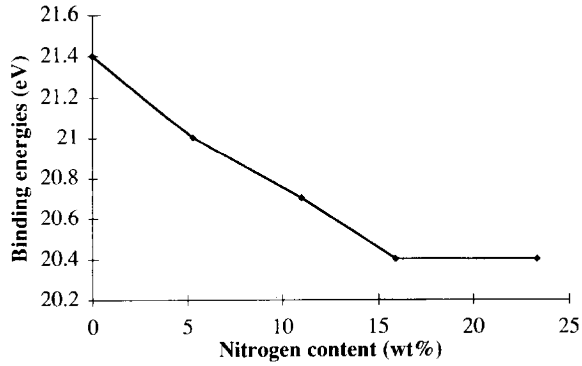

Fig. 3. Evolution of the Ga_{3d} binding energies with the total nitrogen content.

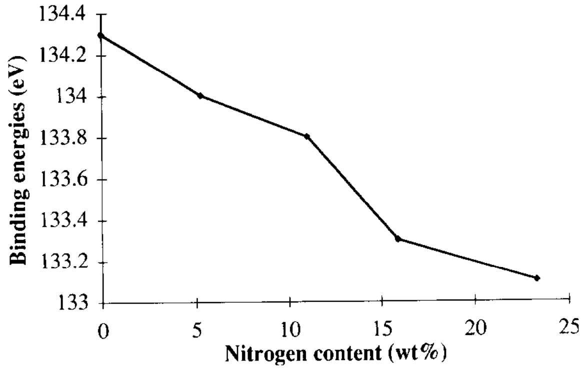

Fig. 4. Evolution of the $P_{2p1/2}$ binding energies with the total nitrogen content.

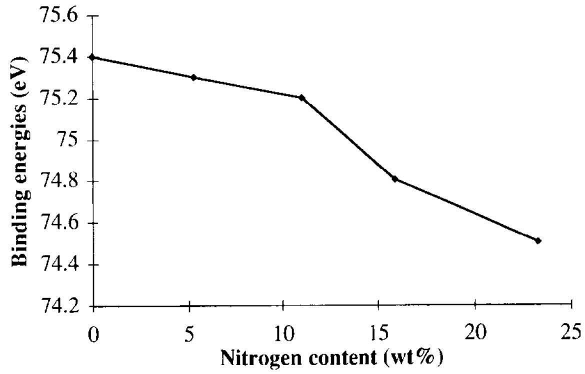

Fig. 5. Evolution of the Al_{2p} binding energies with the total nitrogen content.

4 Conclusions

A series of four oxynitrides of general formula $Al_{0.5}Ga_{0.5}PO_{(8-3y)/2}N_y$, with variable nitrogen content: 5, 11, 16 and 23 wt%N, were obtained by varying only the time of nitridation at 750°C.

Those oxynitrides and the oxide precursor were studied by X-ray photoelectron spectroscopy. One originality of this study is that, as certain gallium Auger and photoelectric peaks superpose, combined analysis with both Al (1486·6 eV) and Mg (1253·6 eV) anodes was done.

From this study, we concluded that:

- the Al_{2p}/N_{1s} atomic ratio evaluated with the Al anode is significantly affected by the N_{1s}–Ga Auger peak superposition and cannot be used for quantitative measurements; with the Mg anode, however, accurate quantification is possible without Ga–Auger photoelectric peak decomposition;
- a good correlation exists between the surface atomic ratios evaluated by XPS and the bulk composition, determined by chemical analysis;
- oxygen substitution by nitrogen occurs

preferentially around gallium and phosphorous atoms, rather than around aluminium. Indeed, oxygen substitution by nitrogen reduces the positive charge around those atoms which decreases their binding energy.

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