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Auger electron spectroscopy of the air-exposed $(Cr_{0.5}Mn_{0.5})_2GaC$ MAX film surface

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We have analyzed chemical bonding of atmospheric oxygen with chromium and manganese on the epitaxial MAX-phase $(Cr_{0.5}Mn_{0.5})_2GaC$ surface using Auger electron spectroscopy combined with ion etching. It was found that the system has a specific anisotropic oxidation where oxygen atoms bind to chromium and manganese ones more actively at the faces of layered MAX phase crystallites in contrast to the (0001) basal plane. At the same time, the dominance of the Mn−O chemical bonding over Cr−O is observed on the latter.

Keywords: MAX phases, Auger electron spectroscopy, epitaxial films, ion etching.

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MAX phases belong to a family of atomically layered ternary compounds with the general formula of $M_{n+1}AX_n$, where M is an early transition metal, A is, in most cases, an element of groups III−V of the periodic table (Al, Si, Ga, Ge, etc.), X is carbon or nitrogen, and $n = 1-3$. Within the wide range of possible MAX materials, the ones attracting special interest are thin films of the $(Cr_{1-x}Mn_x)_2GaC$ ferromagnetic system with $x > 0.3$, wherein the upper Mn concentration threshold typical of the bulk MAX phase may be crossed [1]. Specifically, epitaxial $(Cr_{0.5}Mn_{0.5})_2GaC$ films exhibit ferromagnetic ordering even at room temperature owing to a high Mn concentration [1] while still remaining highly chemically resistant due to Cr−C bonding [2]. The processes of surface oxidation in air of such (Cr, Mn-containing) MAX materials without additional protective coatings remain understudied at present. An insight into these processes could assist in selecting the functional groups for oxygen-terminated Cr, Mn-containing MXenes, quasi-two-dimensional materials that are produced by chemical exfoliation of the MAX phase and removal of component A [3].

The aim of the present study is to analyze the result of oxidation of an atomically layered $(Cr_{0.5}Mn_{0.5})_2GaC$ MAX phase, which was stored in air, by atmospheric oxygen using a combination of Auger electron spectroscopy (AES) and ion etching techniques. Experiments were performed at the Laboratory of Magnetic MAX Materials of the Kirensky Institute of Physics. Two samples of an epitaxial $(Cr_{0.5}Mn_{0.5})_2GaC$ film with a thickness of 12.5 and 40.3 nm, which were synthesized at the Linköping University in Sweden by magnetron deposition onto a MgO(111) substrate, were used. The process of their synthesis was detailed in [4]. Samples were stored for four years under normal conditions (room temperature and a relative humidity of $60 \pm 10\%$) in a room where no research involving acids, alkalies, and other caustic chemicals was performed. According to the scanning electron microscopy data (see Figs. 1, *b* and *d* in [2]), the 12.5-nm-thick MAX film sample has a developed surface with lateral (non-parallel to the MgO(111) plane) faces of textured crystallites constituting a significant fraction of it. The 40.3-nm-thick MAX film sample has a more uniform morphology with predominant basal planes parallel to the MgO(111) surface.

Samples with approximate lateral dimensions of 1.5×2 mm were secured, one after another, onto a holder and annealed in ultrahigh vacuum (UHV) under a base pressure of $5 \cdot 10^{-7}$ Pa at 300°C for 3 h. This annealing was performed in order to remove adsorbed water and clean the surface of samples from organic contaminants that could accumulate there as a result of storage in air. Residual gases were analyzed with an SRS RGA100 mass spectrometer to assess the influence of atomic oxygen and OH hydroxyl ions produced in the process of dissociation of water molecules inside the vacuum chamber during annealing. In the process of heating of samples, the $H_2O/(O+OH)$ ratio of partial pressures remained unchanged to within 10^{-11} Pa. This is indicative of desorption of water molecules without the subsequent dissociation. AES measurements were carried out using an ErLEED 100 (SPECS) system after annealing and cooling of each sample to room temperature. The energy of primary electrons was 3 keV, the electron beam diameter was < 1 mm, the electron emission current was $\sim 0.4\,\mu$A, the accelerating voltage was 660 V, and the spectrum recording step was 0.1 eV. The spectrometer detector was calibrated against Cr and Mn Auger peaks

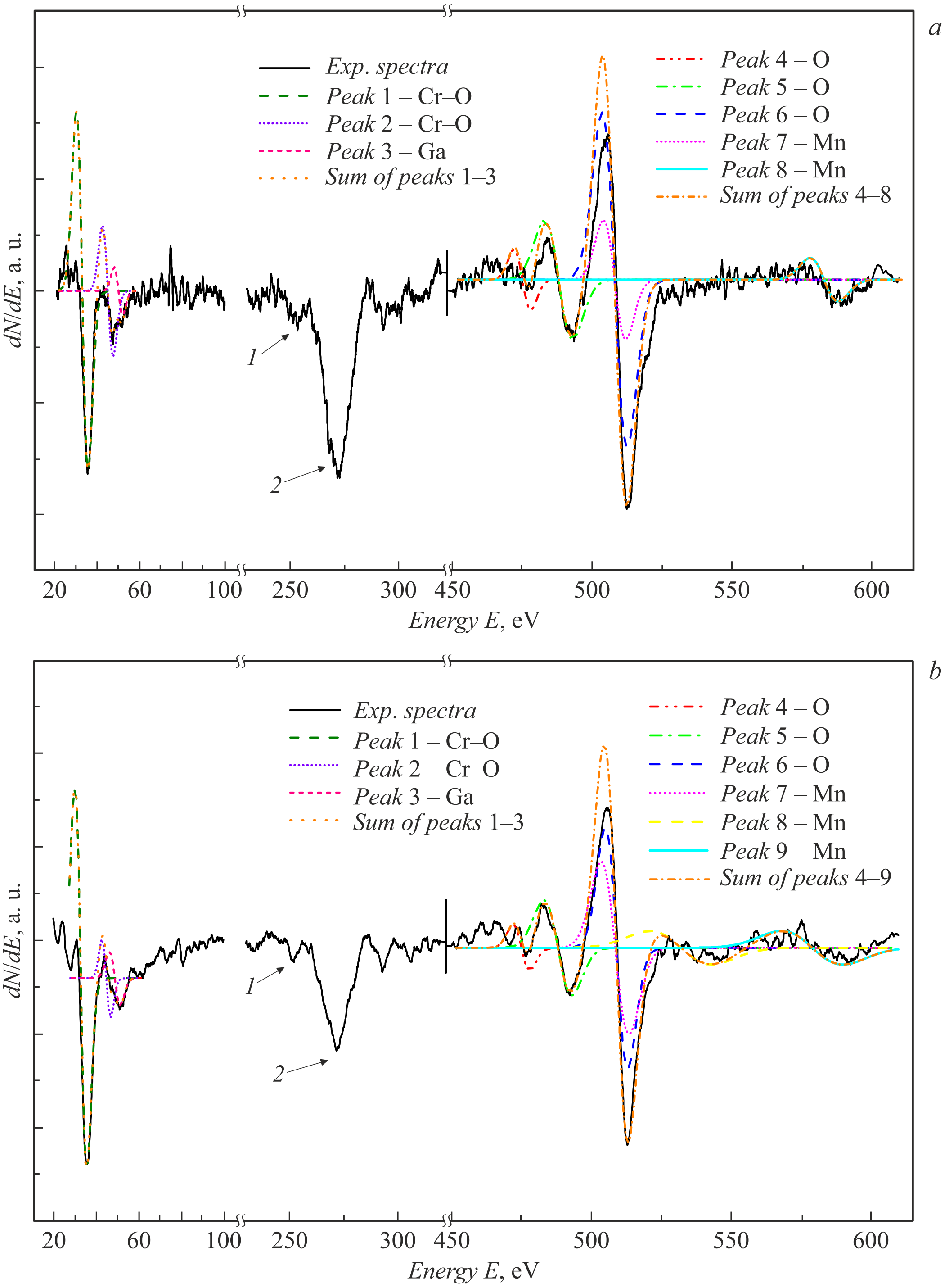

Figure 1. AES data for a sample with a thickness of 12.5 nm before (*a*) and after (*b*) ion etching. Peaks of carbon in the form of carbide are numbered: *1* — 252 eV; *2* — 272 eV. A color version of the figure is provided in the online version of the paper.

with the use of polycrystalline films of these elements with a thickness of approximately 50 nm that were synthesized by magnetron deposition in the UHV chamber from targets with a mass purity of 99.95% immediately prior to the measurement of Auger spectra. Following the measurement of Auger spectra of $(Cr_{0.5}Mn_{0.5})_2GaC$, the samples, which remained in UHV, were etched with argon ions. An ion beam with a diameter of approximately 15 mm was directed at the sample surface at an angle of 60° to the normal. The processed sample was rotated about its axis at a rate of 0.5 rpm. The accelerating voltage of the ion gun was 1.5 kV, and the argon pressure in the chamber was 0.013 Pa. The etching time was 60 min for both samples. As a result of this processing, the $(Cr_{0.5}Mn_{0.5})_2GaC$ film thickness was

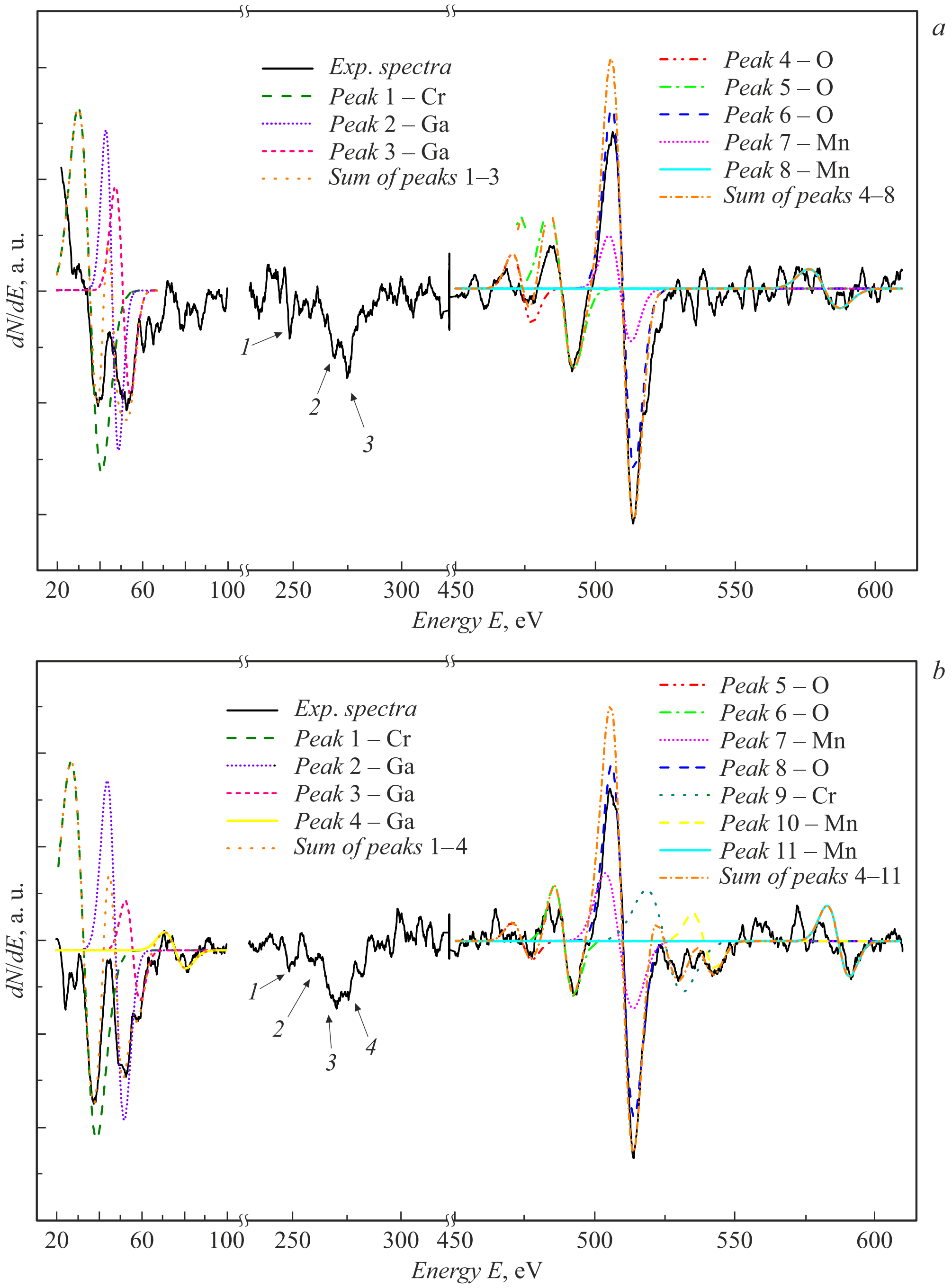

Figure 2. AES data for a sample with a thickness of 40.3 nm before (*a*) and after (*b*) ion etching. Peaks of carbon in the form of carbide are numbered: *a*) *1* — 250 eV, *2* — 271 eV, and *3* — 275 eV; *b*) *1* — 250 eV, *2* — 260 eV, *3* — 271 eV, and *4* — 275 eV. A color version of the figure is provided in the online version of the paper.

reduced by 3 nm on the average (according to the results of preliminary calibration of the etching rate with the use of atomic force microscopy and a photoresist mask).

Following ion etching, $(Cr_{0.5}Mn_{0.5})_2GaC$ samples were annealed again in UHV at 300°C for 30 min to induce argon desorption. At the last stage, Auger spectra were recorded again in the same coordinates at room temperature.

The obtained AES data for both samples after the subtraction of background and the application of a Savitzky–Golay smoothing filter are presented in Figs. 1 and 2. To facilitate detailed data analysis, the results of decomposition of Auger spectra are shown in the same figures. Differential Gaussian peaks used in this decomposition had the form [5]

$$f(x) = y_0 - A(x - x_c)\exp\left(-\frac{(x - x_c)^2}{2w^2}\right)\Big/ w^2, \qquad (1)$$

where A is the integral peak amplitude, x_c is the position of the inflection point of a differential peak in the spectrum,

Table 1. Parameters of fitting differential Gaussian peaks of the Auger spectrum of the sample with a thickness of 12.5 nm

Before etching			After etching		
Peak number	$E_{\min}$, eV	A, a. u.	Peak number	$E_{\min}$, eV	A, a. u.
1	34.5 ± 0.4	10.10 ± 0.11	1	35.74 ± 0.18	12.5 ± 0.3
2	46.41 ± 0.14	3.1 ± 0.2	2	47.5 ± 0.8	1.4 ± 0.2
3	51.22 ± 0.09	0.7 ± 1.2	3	52.0 ± 0.7	1.5 ± 0.3
4	477.9 ± 0.4	1.38 ± 0.09	4	478.4 ± 0.7	2.33 ± 0.13
5	493.39 ± 0.13	9.7 ± 0.2	5	493.2 ± 0.3	9.5 ± 0.5
6	512.57 ± 0.15	25.1 ± 1.2	6	512.7 ± 0.8	16.8 ± 0.4
7	512.44 ± 0.08	7.10 ± 0.14	7	513.7 ± 0.4	9.8 ± 0.7
8	588.1 ± 0.5	3.0 ± 1.0	8	542.9 ± 1.7	15.6 ± 0.9
			9	590.4 ± 1.4	20.2 ± 0.9

Table 2. Parameters of fitting differential Gaussian peaks of the Auger spectrum of the sample with a thickness of 40.3 nm

Before etching			After etching		
Peak number	$E_{\min}$, eV	A, a. u.	Peak number	$E_{\min}$, eV	A, a. u.
1	40.9 ± 1.6	65.1 ± 1.8	1	39.0 ± 0.6	60.0 ± 1.4
2	49.4 ± 1.4	17.1 ± 0.7	2	51.9 ± 0.3	24.0 ± 1.1
3	54.6 ± 1.7	14.9 ± 0.9	3	59.4 ± 0.6	5.4 ± 0.8
4	477.9 ± 0.6	4.9 ± 0.3	4	81.2 ± 1.8	3.9 ± 1.4
5	492.4 ± 0.2	18.4 ± 0.4	5	477.7 ± 1.8	1.8 ± 0.3
6	514.00 ± 0.08	33.7 ± 0.3	6	492.4 ± 0.5	5.9 ± 0.2
7	512.6 ± 0.3	9.4 ± 1.1	7	513.7 ± 0.6	14.7 ± 0.3
8	588.1 ± 1.1	7.2 ± 0.5	8	514.17 ± 0.09	25.7 ± 0.6
			9	531.3 ± 0.3	18.8 ± 0.7
			10	542.7 ± 0.6	4.1 ± 0.3
			11	591.1 ± 0.9	4.4 ± 0.3

and w is the energy from the inflection point of a differential peak to the point of the minimum amplitude.

Energies $E_{\min}$ of Auger peaks were determined as the positions of minima of differential fitting peaks in the following way: $E_{\min} = x_c + w$. The parameters of fitting peaks for samples with a thickness of 12.5 and 40.3 nm are listed in Tables 1 and 2, respectively. The initial parameters and the number of fitting peaks were chosen by finding the best fit between the shape of experimental spectra and curves characterizing the sum of fitting peaks. Fitting was continued until the errors of parameters A, x_c, and w reached their minimum.

The obtained decomposition reveals that the high intensity of the peak around 513 eV in the spectra of both samples is the result of overlapping of manganese and oxygen peaks with close energies [6–8]. The energy of the Auger peak of manganese for the sample with a thickness of 12.5 nm (peak 7 in Table 1) increases by 1.3 ± 0.4 eV after etching due to the breaking of chemical bonds between manganese and oxygen [9]. The energy of Auger peaks of manganese in the spectra of the sample with a thickness of 40.3 nm (peak 7 in Table 2) varies in a similar manner: following ion etching, it increases by 1.1 ± 0.7 eV. Auger peaks of manganese and chromium (peaks 9 and 10 in Table 2) also became identifiable after ion etching. It was also found that the energy of Auger peaks of manganese of the $(Cr_{0.5}Mn_{0.5})_2GaC$ MAX phase is generally lower than the corresponding energy for a pure polycrystalline metal film. Relying on the data from [10] and the fact that Ga and Ge belong to the same class of components A of MAX phases, one may attribute the shift of Mn peaks toward lower energies to the formation of a chemical bond between Mn, Ga, and C.

It was demonstrated in [11] that Auger spectra of chromium change when chromium oxide Cr_2O_3 forms. Specifically, the Auger peak of chromium in the low-energy region shifts toward lower kinetic energies, and a second (additional) higher-energy peak emerges at a distance of 13 eV from the major one. Peaks with an energy of approximately 35 and 47 eV (peaks 1 and 2 in Table 1) are seen in the spectra of the sample with a thickness of 12.5 nm. According to [11], this is indicative of Cr$-$O bonding. It turned out to be impossible to decompose the low-energy region of the experimental spectrum of the sample with a thickness of 40.3 nm into four peaks that would be similar to those for the 12.5-nm-thick sample. This indicates a lack of Cr–O bonding. It was also found that the energy of Auger peaks of chromium in the spectra of the sample with a thickness of 40.3 nm after ion etching (peaks 1 and 9 in Table 2) is higher than the corresponding energy for pure chromium (36.9 and 530.4 eV). These changes may be the result of a reduction in the electron–core binding energy in Cr atoms due to the formation of chemical bonds with Mn, Ga, and C atoms.

Auger peaks of carbon around 275 eV, which are typical of carbides [12], are seen in the spectra of both samples recorded before and after etching. The minimum of the major carbon peak is split clearly into two peaks in the spectra of the sample with a thickness of 40.3 nm (Fig. 2), thus indicating the formation of chromium carbides [13,14]. This „splitting" of the peak is also manifested (in the form of asymmetry of its slopes) in the spectrum of the 12.5-nm-thick sample. Peak 3 in the spectrum of the 12.5-nm-thick sample after ion etching (Table 1) and peaks 2–4 in the spectrum of the 40.3-nm-thick sample after ion etching (Table 2) are identified as weak Auger peaks of gallium [6–8]. In our view, the mismatch between their energies in two samples is caused by differences in the chemical environment or by the formation of bonds with oxygen. Owing to the lack of literature data, the validity of these assumptions cannot be verified.

Summarizing the above, one may note that the spectra of both samples measured prior to ion etching contained only those peaks of manganese that correspond to its chemical bonding with oxygen. The residual shift of Mn peaks to energies lower than those corresponding to a pure metal may be attributed to the formation of a chemical bond between Mn, Ga, and C. We failed to obtain data on bonding of manganese with other elements owing to the possible chemical affinity of Mn and Cr atoms in the M layer of the $(Cr_{0.5}Mn_{0.5})_2$GaC MAX phase. As for chromium, the signs of its chemical bonding with oxygen were identified only in the spectra of the 12.5-nm-thick film measured both before and after etching. This suggests that chromium oxidizes in air only within the lateral faces of epitaxial $(Cr_{0.5}Mn_{0.5})_2$GaC MAX film crystallites, which surface area is substantial in the 12.5-nm-thick sample; within the basal plane, oxygen binds predominantly to Mn atoms. It follows from the values of sputtering yields for chromium and manganese reported in [15] that the instantaneous sputtering rate for manganese is approximately 1.5 times higher. This is the reason why bonds Mn–O break and Cr–O bonds are preserved through the ion etching of a porous MAX layer of the 12.5-nm-thick sample. The method of decomposition of Auger spectra into differential Gaussian peaks made it possible to identify the difference between the results of oxidation of $(Cr_{0.5}Mn_{0.5})_2$GaC MAX films with a varying surface morphology and provided the needed data to conclude that their oxidation is anisotropic in nature.

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Conflict of interest

The authors declare that they have no conflict of interest.

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