

XPS and AES Studies on the Oxidation Process of Layered Semiconductor GaSe

Hiroaki IWAKURO,^{*} Chiei TATSUYAMA and Shoji ICHIMURA
*Department of Electronics, Faculty of Engineering,
Toyama University, Takaoka, Toyoma*

The oxidation process of layered compound GaSe which has no dangling bond on the cleaved surface has been studied by XPS and AES techniques. At room temperature, the cleaved surface is not oxidized in oxygen gas atmosphere. By Ar ion sputtering, the surface becomes to show the behavior of metallic Ga due to the dissipation of the first sublayer of Se in a primitive layer Se-Ga-Ga-Se. The thin layer of the metallic Ga is easily oxidized. In the case of thermal oxidation of cleaved GaSe in air atmosphere, the oxygen diffuses into the primitive layer and combines with Ga, which causes the severance of the intralayer bonding between Se and Ga atoms. At temperature higher than 450°C, the oxygen is also intercalated between the primitive layers from the sides perpendicular to the layers. No Se oxides are observed under any of the oxidation conditions.

§ 1. Introduction

The use of x-ray photoemission spectroscopy(XPS) is a powerful technique for the study of the electronic structures of atoms, molecules and condensed matter¹⁾. The most dramatic success of XPS is to give the informations concerning the bonding of atoms or molecules to the surface through the observation of the so called chemical shift.

The GaSe has a layered structure consist of stacking of primitive layer with four sublayers of atoms in the sequence Se-Ga-Ga-Se as shown in Fig.1. The difference in the stacking sequence of primitive layers yields three polytypes, ϵ , β and γ ²⁾. The hexagonal unit cell of ϵ type, which is usually appeared in GaSe, extends over two primitive layers. The lattice constant c along the stacking is 15.94 Å, which includes two primitive layers(9.56 Å) and two inter layer spacings(6.38 Å)³⁾. Within the primitive layer the bonding is a strong covalent type, whereas between the primitive layers it is a weak van der Waals type. The electrical and optical properties of GaSe related to the anisotropy of the bonding strength have been extensively studied for many years.⁴⁾ The crystal can be cleaved readily against the weak inter-layer bonding. The cleaved surface is considered to be relatively inert, since no dangling bonds exist on the surf-

^{*} Present address: The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565.

ace. On the other hand, the surface of usual 3-dimensional crystals gives rise to dangling bonds inevitably.

We are interested in the interactions between atoms or molecules and the surface without dangling bond. Recently, it has received much attention that the weak inter layer bonding of layered structures facilitates the intercalation of fo-

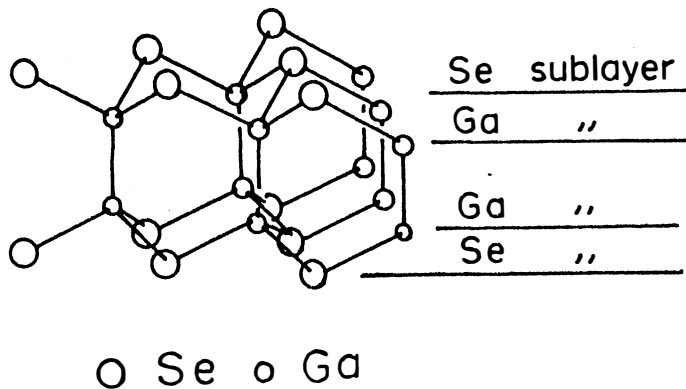


Fig. 1 Primitive layer of GaSe.

reign atoms or molecules between the primitive layers under suitable conditions^{5,6)}. The intercalation sometimes changes dramatically the properties of the host materials. The opto-electronic devices using GaSe and InSe heterostructured with SnO₂ have also been interested^{7,8)}.

In the present paper, we will focus on the study of the oxidation process of GaSe observed by means of XPS and AES (Auger electron spectroscopy) techniques. The oxide layer on the surface of typical semiconductor, such as Si⁹⁾ and GaAs¹⁰⁾, has been widely studied, since it has a large effect on the characteristics of the devices made from these materials. However, the oxidation of the layered materials has not yet been studied, at least to our knowledge.

§ 2. Experimental

The GaSe single crystals used for the present study were grown from the melt sealed in a quartz ampule by the Bridgman method. The crystal was *p*-type, and mobility and carrier concentration at room temperature were $\sim 30 \text{ cm}^2/\text{volt}\cdot\text{sec}$ and $\sim 10^{15} \text{ cm}^{-3}$, respectively. The single crystal ingot with diameter $\sim 12 \text{ mm}\phi$ was cleaved into thickness of $\sim 0.5 \text{ mm}$ in the argon gas passed through dry system. The thermal oxidation of the samples was performed on an iron plate heated in air atmosphere.

The experimental equipment consisted of the PHI Model 548SH ESCA/Auger system with a double pass cylindrical mirror type analyzer (CMA) in the ULVAC high vacuum chamber (10^{-9} Torr). The vacuum system has a small subchamber where the sample can be exposed to appropriate gas atmosphere keeping the main chamber at high vacuum. The room temperature oxidation was performed in the subchamber. The oxidized sample is carried into main chamber for measurement by the driving system. The equipment also enables us to measure SIMS (secondary ion mass spectroscopy) and RHEED (reflection high energy electron diffraction), although these were not used for the present experiment.

The oxidation processes were observed by the measurement of the chemical shifts of photoemission lines due to Se 3*d*, Ga 3*d* and O 1*s* core electrons and Ga ($L_{3M_{45}M_{45}}$)

Auger transition. The binding energies of these lines in oxidized samples were compared with those in standard materials, Se, Ga, SeO_2 , Ga_2O_3 and cleaved GaSe. The unmonochromatized Mg-K α X-ray (1253.6 eV) operated at 10 kV and 40 mA was used as the excitation source. In Se atoms, the strongest line is Se(L₃M₄₅M₄₅) Auger line, but the kinetic energy is higher than the energy of Mg-K α X-ray. The binding energies were calibrated to the Au 4f_{7/2} (83.8 eV) line whose FWHM (full width at half maximum) was 1.2 eV. The experimental accuracies for the determination of the binding energy and FWHM were estimated to be ± 0.2 eV and ± 0.1 eV, respectively.

The Ar ion sputtering was performed for the depth profile of the elemental composition in oxidized samples. The elemental composition was measured as a function of sputtering time by AES. An argon ion gun was operated at a voltage 5 kV and an emission current 30 mA in an argon gas pressure of 5×10^{-5} Torr, which resulted in a sputtering rate of about 33 Å/min for evaporated GaSe. This sputtering rate was used as an approximate value for the oxidized samples. For the AES measurement, a primary beam energy was 3 kV and a modulation of the signal was 6 eV in peak to peak. The relative sensitivity in the present system was estimated to be 0.36, 1.0, 0.59 and 0.33 for C(KLL), O(KLL), Ga(LMM) and Se(LMMM) Auger lines, respectively.

§ 3. Results and Discussion

3-1 Standard materials

In this section, the binding energies of the typical photoemission lines of standard materials, Ga, Se, Ga_2O_3 , SeO_2 and cleaved GaSe (hereafter referred to as *cl*-GaSe) are determined. The surface of Ga metal was etched by Ar ion sputtering before measurement. The Se, Ga_2O_3 and SeO_2 were powdered samples. The GaSe was cleaved in Ar gas. The Au was evaporated on the samples for the calibration of the binding energies.

Table 1 shows the measured binding energies of Ga 3d, Se 3d, O 1s and Ga(L₃M₄₅M₄₅) lines, where the binding energy of Ga(L₃M₄₅M₄₅) means the energy difference between the energy of Mg-K α X-ray and the kinetic energy of the Auger electron. The binding energies of Ga 3d and Ga(L₃M₄₅M₄₅) in Ga metal are 18.7 and 185.7 eV, respectively. The former value well agrees with the result by Schön (18.5 \pm 0.2 eV)¹¹⁾. Those of Se 3d in Se and SeO_2 are 54.7 and 58.6 eV, the value for Se coincides with that of Weser et al. (54.8 eV)¹²⁾, but the value for SeO_2 is smaller than their result by about 0.5 eV.

The values of Ga 3d, Ga(L₃M₄₅M₄₅) and O 1s in Ga_2O_3 are 20.3, 191.0 and 531.1 eV, which are in agreement with results by Mizokawa et al. (20.4 \pm 0.2, 191.1 \pm 0.2, 531.4 \pm 0.2)¹³⁾ and Schön (20.5 \pm 0.2, —, 531.1 \pm 0.2 eV)¹¹⁾. In Ga_2O_3 , the FWHM of lines was wider than in other materials, and the Ga 3d line was decomposed into five Gaussian lines with FWHM 1.3 eV as shown in Table 1. The main peak at 20.3 eV is due to Ga_2O_3 . The weak peak at 18.7 eV agrees with the peak of Ga metal. The other lines show the presence of higher (21.6 and 23.0 eV) and lower (19.3 eV) oxidation states of Ga than Ga_2O_3 .

Table 1 Binding energies in eV of Ga 3d, Se 3d, Ga(L₃M₄₅M₄₅) and O 1s in the samples. For the oxidized samples, see the captions of Figs.2 and 6. The binding energy has an uncertainty of ± 0.2 eV. The Ga 3d in the several samples are decomposed into a few Gaussian lines with FWHM 1.3 eV, in wich the strong line is marked by s. The energy of Ga(L₃M₄₅M₄₅) in parenthesis is observed only as a shoulder.

	Ga 3d	Se 3d	Ga(L ₃ M ₄₅ M ₄₅)	O 1s
Ga	18.7		185.7	
Se		54.7		
Ga ₂ O ₃	18.7			
	19.3			
	20.3 s		191.0	53.1.1
	21.6			
	23.0			
SeO ₂		58.6		530.5
<i>cl</i> -GaSe	19.7	54.4	188.2	
<i>RT</i> -GaSe(b)	19.7	54.4	188.2	
<i>sp</i> -GaSe(sp)	18.7 s		185.7	
	19.5 s	54.7	187.8	
<i>sp</i> -GaSe(d)	18.4			
	19.1 s			
	19.5 s	54.7	188.0	
	20.1 s		(191.0)	531.1
	21.1			
<i>T</i> -GaSe(c)	19.6 s	54.7	188.3	531.2
	20.2 s		(191.0)	
	21.3			
<i>T</i> -GaSe(e)	19.3			
	20.5 s		191.2	531.2
	21.8			
	23.0			

The peak energies of Ga 3d, Se 3d and Ga(L₃M₄₅M₄₅) lines in *cl*-GaSe are 19.7, 54.4 and 188.2 eV, respectively. The values reported by Antonageli et al⁽⁶⁾ for Ga 3d and Se 3d are 19.4 and 45.3 eV, which are measured from the top of valence band of GaSe. The difference of binding energy of Se 3d between in GaSe and SeO₂ is large as 4.2 eV, which is convenient to distinguish Se-oxides from GaSe. On the other hand, the energy differences of Ga(L₃M₄₅M₄₅) are 2.5 and 2.8 eV for (GaSe-Ga) and (Ga₂O₃-GaSe), which are useful for the observation of Ga-oxides on the surface of GaSe.

3-2 Room temperature oxidation

Figur 2 shows the XPS spectra of Ga 3d in the samples oxidized at room temperature, where the spectra a and b are obtained from the samples(referred to as *RT*-GaSe) exposed to oxigen gas of one atm for 1 and 9 hours, respectively, after cleaving, and sp, c and d are the spectra in the samples(referred to as *sp*-GaSe)exposed to oxigen gas of one atm for 0, 1, and 60 minutes, respectively, after Ar ion sputtering of 20 minutes.

Figures. 3 and 4 show the corresponding spectra of Se 3d and Ga(L₃M₄₅M₄₅) in the same samples as Fig.1. The spectra a and b in the three figures are just the same as *cl*-GaSe, which indicates the surface of GaSe is quite stable in oxygen atmosphere as room temperature.

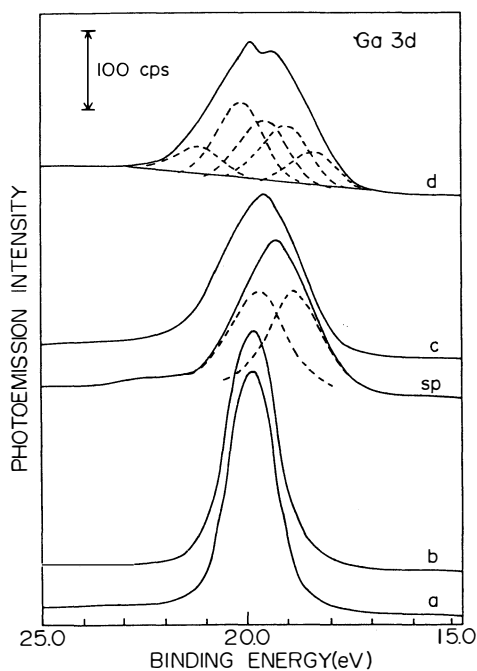


Fig.2 XPS spectra of Ga 3d in *RT*-GaSe (a, b) and *sp*-GaSe, a and b were exposed to oxygen gas of one atm pressure for 1 and 9 hours without sputtering, and sp, c, and d were exposed to oxygen gas for 0, 1 and 60 minutes after Ar ion sputtering, respectively.

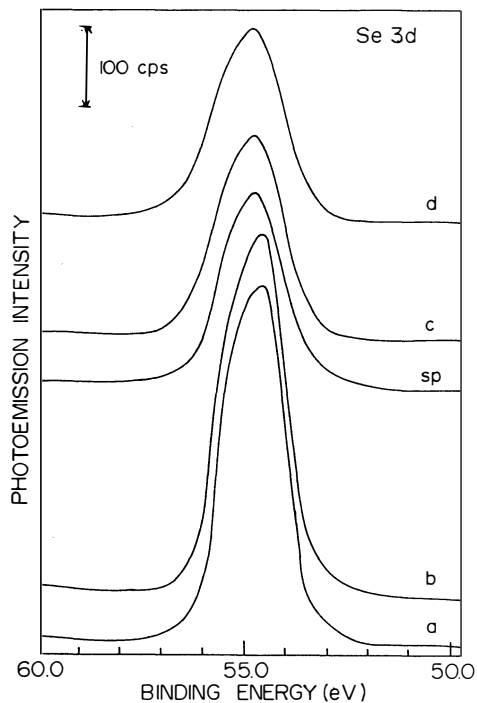


Fig.3 XPS spectra of Se 3d in *RT*-GaSe and *sp*-GaSe. The samples are the same as Fig.2.

As seen from the spectra *sp* in Figs. 2, 3 and 4, the sputtering makes the signal broader for all photoemission lines. The relative integral intensity of Se 3d to Ga 3d decreases from 2.0 in *cl*-GaSe to 1.0 in *sp*-GaSe without exposure to oxygen, which demonstrates that the surface becomes Ga-rich by Ar ion sputtering. The spectrum *sp* of Ga 3d in Fig.2 is decomposed into two Gaussian lines with FWHM 1.3 eV centered at 19.5 and 18.7 eV, one of which (18.7 eV) coincides with the energy of Ga metal (see also Table 1). The other peak at 19.5 eV is due to

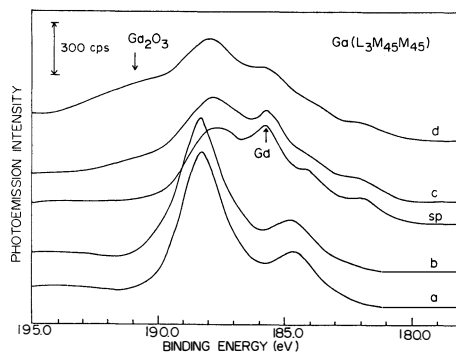


Fig.4 XPS spectra of Ga(L₃M₄₅M₄₅). The samples are the same as Fig. 2.

GaSe, the energy is slightly lower than in *cl*-GaSe. The existence of Ga metal on the sputtered surface is clearer from the spectrum *sp* shown in Fig. 4, where the peak marked by an arrow(↑) corresponds to Ga metal. The Ga(L₃M₄₅M₄₅) in GaSe is shifted to lower energy by about 0.4 eV compared with *cl*-GaSe. On the other hand, the binding energy of Se 3*d* is shifted to higher energy by about 0.3 eV as shown in Fig. 3 and Table 1.

The metallic nature of the sputtered surface may be due to the dissipation of the first sublayer of Se atoms in a primitive layer. The Ga atoms in the second sublayer combine with each other, which results in the formation of metallic Ga. We think the bonding between the Ga atoms in the third layer and Se atoms in the fourth sublayer is still present on the surface, which may be the origin of the observed shifts of binding energies by sputtering mentioned above. We note here that all of the energies of Ga 3*d*(19.5 eV), Se 3*d*(54.7 eV) and Ga(L₃M₄₅M₄₅) (187.8 eV) in *sp*-GaSe are closer to those of elemental Ga and Se than those in *cl*-GaSe.

In the case of *sp*-GaSe, the signals corresponding to Ga oxides begin to appear with increase of exposure time to oxygen, in contrast to the case of *RT*-GaSe. The spectrum *d* of Ga 3*d* is decomposed into five lines as shown in Fig. 2. The peak energies of the five lines are shown in Table 1, where

the energies of 18.4, 19.5 and 20.1 eV almost agree with those of Ga 3*d* in Ga, *sp*-GaSe and Ga₂O₃, respectively. The other two peaks at 19.1 and 21.1 eV may be due to the lower and higher oxidation states of Ga than Ga₂O₃. The situation is very similar to standard Ga₂O₃, except for the difference in the that of relative intensities of the decomposed lines.

From the spectra of Se 3*d* in Fig. 3, we know that Se-oxides are not formed, even if *sp*-GaSe is exposed to oxygen for 60 minutes at room temperature. This is also clear from the binding energy of O 1*s* shown in Table 1, which agrees with the energy in Ga₂O₃.

Figure 5 shows the depth profile of the elemental composition of *sp*-GaSe oxidized for 1 minute measured by AES as a function of Ar ion sputtering time. The summation of the peak to peak heights of AES signals for Se, Ga, O and C atoms corrected by relative sensitivity is normalized to 1. In the figure, the intensities of oxygen peak in the samples exposed for 10(drawn by ---) and 60 minutes(drawn by —) are also shown. As seen from the figure, the

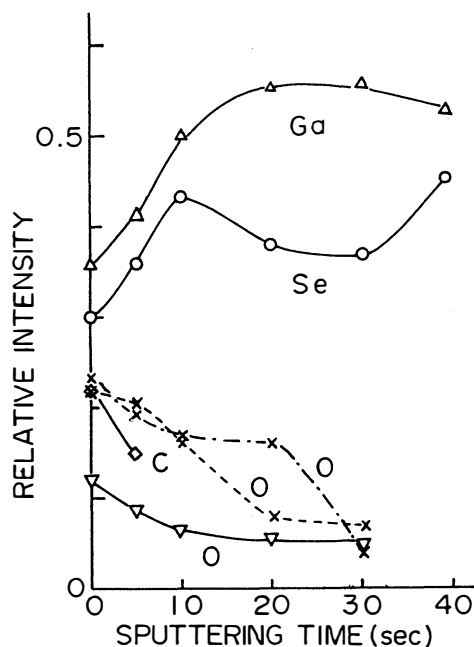


Fig. 5 Depth profile of elemental compositions in sample .c in Fig. 2. Dotted curve(---) and broken curve(—) represent the oxygen intensity in the sputtered samples exposed to oxygen for 10 and 60 minutes, respectively.

intensity of Ga is always stronger than that of Se, which indicates the surface is Ga-rich. The oxygen peak disappears after 30 sec. sputtering for all exposure times. The depth of the existence of oxygen does not depend on the exposure time. The results show that the oxidation layer is formed only for the layers damaged by sputtering. If we assume the sputtering rate of 33 Å/min for evaporated GaSe is used for the present samples, the depth of oxide layer is calculated to be about 16 Å, which is about the same to the thickness of two primitive layers of GaSe.

3-3 Thermal oxidation

Figures 6, 7 and 8 show the spectra of Ga 3d, Se 3d and Ga(L₃M₄₅M₄₅) in the samples (referred to as T-GaSa) oxidized at several temperatures for ten minutes in air atmosphere after cleavage. The oxidation temperatures are 50, 150, 230, 280, and 450°C for the samples a, b, c, d and e, respectively.

As seen from the spectra of Ga 3d in Fig. 6, the intensity of Ga oxides increases with increase of oxidation temperature. The higher energy tail of spectrum b is due to the component of Ga₂O₃. At 230°C, the intensity of Ga₂O₃ becomes almost comparable to that of GaSe as shown in spectrum c. Above 230°C, the component of Ga₂O₃

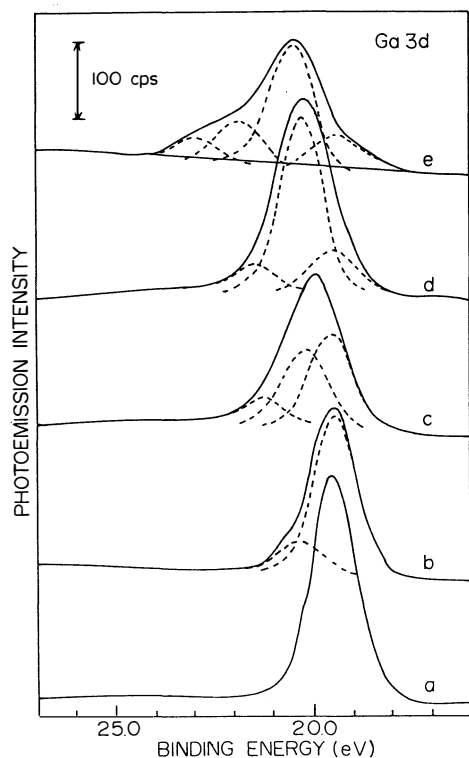


Fig. 6 XPS spectra of Ga 3d in T-GaSe. The oxidation temperatures are 50(a), 150(b), 230(c), 280(d) and 450°C(e).

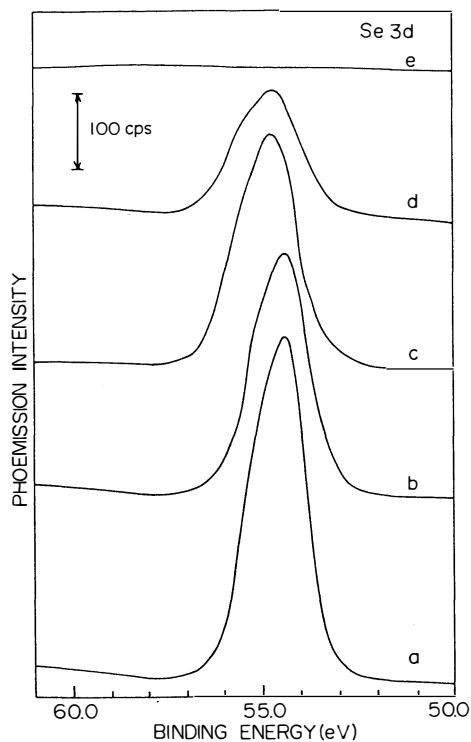


Fig. 7 XPS spectra of Se 3d in T-GaSe. The samples are the same to Fig. 6.

exceeds the GaSe. In the case of 450°C (spectrum e), the signal of Ga 3d consists of four components corresponding to Ga₂O₃ (20.5 eV), GaSe (19.3 eV) and higher oxidation states of Ga (21.8 and 23.0 eV). The peak at 19.3 eV might be due to lower oxidation state of Ga. The increase of Ga oxides with increase of temperature is also clear from the spectral change of Ga(L₃M₄₅M₄₅) in Fig. 8.

The energy position of Ga (L₃M₄₅M₄₅) in Ga metal is shown in Fig. 8 by the arrow (↓). We should note that the peak corresponding

to Ga metal is not seen in contrast with *sp*-GaSe and its room temperature oxidation. This is also true in the spectra of Ga 3d in Fig. 6 (see also Table 1).

In the case of Se 3d in Fig. 7, the peak energy and FWHM of spectrum a are in agreement with those of *cl*-GaSe. At higher temperature, the signal intensity decreases, and the peak energy is shifted to higher energy by about 0.3 eV accompanied by the slight increase of FWHM. At temperature higher than 450°C, the signal of Se 3d is no more seen as shown in spectrum e. The Se oxides do not appear for all of the oxidation temperatures.

From the above results, the thermal oxidation process of cleaved GaSe is explained as follows. First, the oxygen diffuses into the primitive layer through the first Se sublayer, and combines with Ga atoms of second sublayer. With progress of oxidation, the oxygen atoms combines also with Ga atoms of third sublayer. The formation of Ga oxides causes the break down of the bonding between Se and Ga atoms in the primitive layer. The Se atoms have no bonding with Ga and O atoms, which may be the reason of the shift of binding energy of Se 3d to higher energy and the increase of FWHM. Ga atoms have no bonding with Se atoms present only as Ga oxides, so the signals of metallic Ga are not appeared. At higher oxidation temperature, Se is also combined with oxygen atoms. However, the vapour pressure of Se oxides is very high, for example SeO₂ sublimates at higher than 100°C. This may be the reason why Se oxides are not observed, and the signal of Se 3d becomes smaller with temperature. Thus, the surface is now covered with Ga oxides only.

Figure 9 shows the depth profiles of oxygen measured by AES in the same samples as in Figs. 6, 7 and 8, where Se, Ga and C are not shown. In the samples b, c, and d oxidized at 150, 230 and 280°C, respectively, the oxygen concentration decreases with sputtering time (time scale is in sec.), and it disappears after at most 100 seconds sputtering. On the other hand, in the sample i oxidized at 450°C, the oxygen also decreases for 60 minutes, but after the time, it keeps constant values. This result indicates that at lower temperature the oxidation proceeds from the surface, but at higher temperature the oxidation proceeds not only from the surface, but also through the inter

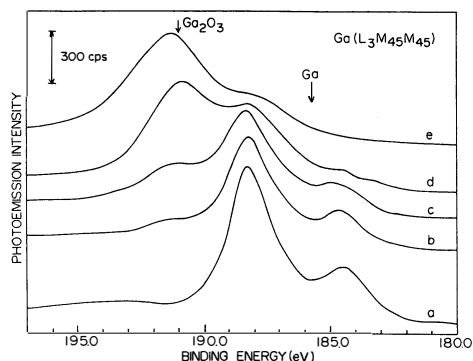


Fig. 8 XPS spectra of Ga(L₃M₄₅M₄₅) in T-GaSe. The samples are the same as Fig. 6

layer. The oxidation through the inter layer means that the oxygen is intercalated between the primitive layers due to the weak bonding between the layers.

§ 4. Summary and Conclusion

We have studied the oxidation process of GaSe by XPS and AES techniques. The cleaved surface of GaSe has been found to be quite stable under oxygen atmosphere at room temperature. The result is a striking feature in contrast to the surface of 3-dimensional crystals which is usually covered by thin oxide layer. This due to the fact that the cleaved surface of GaSe has no dangling bond.

On Ar ion sputtering, the cleaved surface becomes Ga-rich. The XPS spectra show the presence of metallic Ga on the sputtered surface, which is easily oxidized at room temperature. The oxide layer is formed only for the layers damaged by sputtering. No Se oxides are found.

During thermal oxidation in air atmosphere, the intralayer Se-Ga bondings are broken down by the formation of Ga oxides. Se atoms are present simply as selenium. At higher thermal oxidation temperature, the surface almost consists of Ga oxides, mainly Ga_2O_3 . Se oxides sublime due to its high vapor pressure. In the samples heated to temperature higher than 450°C , two types of distribution of oxygen have been found. The one is the decreasing distribution with depth from the surface, which is due to the diffusion of oxygen, and the other is the constant distribution, which is due to the intercalation of oxygen between the primitive layers.

Note: This work has been published in "Jpn. J. Appl. Physics, vol. 21 No.1(1982)"

References

- R. H. Williams, G. P. Srivastava and I. T. McGovern: Rep. Prog. Phys. 43(1980) 87.
- (2) *Physics and Chemistry of Materials with Layered Structures, vol.5, Structural Chemistry of Layer-Type Phases*, ed. by F. Levy(D. Reidel, Dordrecht, 1979)p. 146.
- (3) A. Kuhn, A. Chevy and R. Chevalien: Phys. Status Solidi 31a(1975) 469.
- (4) *Physics and Chemistry of Materials with Layered Structures, vol.4, Optical and Electrical Properties*, ed. by P. A. Lee(D. Reidel, Dordrecht, 1979).
- (5) *Physics and Chemistry of Materials with Layered Structures, vol.6, Intercalation Compound*, ed. by F. Levy(D. Reidel, Dordrecht, 1979).
- (6) S. Ichimura, C. Tatsuyama and O. Ueno: Proc. Int. Conf. Phys. Chem. of

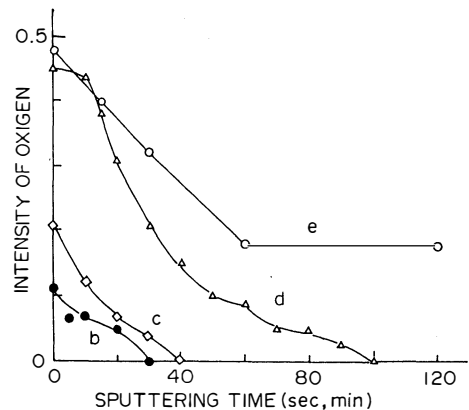


Fig. 9 Depth profile of oxygen in T-GaSe. The samples are the same to Fig.6 Time scale is sec for b, c, d, and min for e.

Layered Materials(Sendai, 1980), to be published in *Physica B*(1981).

- (7) C. Tatsuyama and S. Ichimura: *Japan. J. Appl. Phys.* 15(1976) 843.
- (8) T. T. Nang, T. Matsushita, M. Okuda and A. Suzuki: *Japan. J. Appl. Phys.* 16 (1977) 253.
- (9) I. T. McGovern, A. Parke and R. H. Williams: *Solid State Commun.* 26(1978) 21.
- (10) H. Iwasaki, Y. Mizokawa, R. Nishitani and S. Nakamura: *Japan. J. Appl. Phys* 17(1978) 1925.
- (11) G. Schön: *J. Elect. Spectroscopy* 2(1973) 75.
- (12) U. Weser, G. Sokolowski and W. Pilz: *J. Elect. Spectroscopy* 10(1977) 429.
- (13) Y. Mizokawa, H. Iwasaki, R. Nishitani and S. Nakamura: *J. Elect. Spectroscopy* 14(1978) 129.
- (14) F. Antonangeli, M. Piacentini, A. Balzarotti, V. Grasso, R. Girlanda and E. Doni: *Nuovo Cimento* 51B (1979) 181.

(Received November 20. 1981)