Phase formation in surface layers of GaTe and InTe single crystals during thermal oxidation in air

O.A.Balitskii, V.P.Savchyn, P.V.Savchyn, Ya.M.Fiyala

Department of Electronics, Lviv I.Franko National University, 50 Drahomanov Str., 79005 Lviv, Ukraine

Received November 18, 2004

The oxidation processes of indium and gallium monotellurides have been discussed. The oxidation has been established to result in formation of additional phases with higher tellurium content, namely, gallium and indium sesquitellurides, respectively.

Исследован фазовый состав приповерхностных слоев термически оксидированных на воздухе монокристаллов GaTe и InTe. Установлено, что оксидирование сопровождается образованием дополнительно фазы с большим содержанием теллура — полуторателлуридов галлия и индия соответственно.

Recently, the indium and gallium monotellurides have been used in semiconductor heterostructures creation [1, 2]. Furthermore, their formation at the interface is typical of structures of $A^{II}B^{VI}/A^{III}B^{V}$ type [3, 4].

Thermal oxidation of semiconductor crystals is one of the most often used methods to create heterostructures for different practical applications. The chemical composition of semiconductor/intrinsic oxide interface for all phases is a key factor controlling properties of such structures. The oxidation processes are well studied for many semiconductors, in particular, for elemental ones. However, the structure and phase composition of oxidized layers have not been described to date for tellurides of 3rd Group metals. The main difficulty in description of A^3B^6 compounds oxidation is a possibility of several stable phases in contrast, for example, to A^2B^6 and A^4B^6 systems. So, the Ga–Te system has three stable phases (GaTe, Ga_2Te_3 and Ga_2Te_5) [5] while the In–Te system has four ones (In_4Te_3, InTe, In_2Te_3 and In_2Te_5) [6]. In connection with uncertainty of intrinsic oxide formation on surfaces of A^3B^6 compounds, this work is devoted to the study of physical and chemical processes of oxygen interaction with InTe and GaTe single crystals cleavages.

GaTe and InTe single crystals were grown by Bridgman method from previously synthesized alloys. The thermal oxidation of samples was carried out by heat treatment in an electric furnace in air. The samples have been brought into the furnace previously heated to the specified temperature for a specified time to guarantee fast heating. During the heat treatment, the temperature was maintained at an accuracy to within ±3°C. The cathodoluminescence (CL) analysis and of X-ray diffraction (XRD) have been chosen to study the intrinsic oxide layer composition. The XRD patterns were recorded using a DRON-3 spectrometer in the range of 20–80° with a scan step of 0.05° using monochromatic radiation from Cu–K_α X-ray source. The phases were identified by their individual XRD data [7]. The CL was excited at nitrogen temperature by electron pulses of 3 μs duration, 20 Hz frequency, a current in the electron beam of 200 μA, electron energy 9 keV and electron

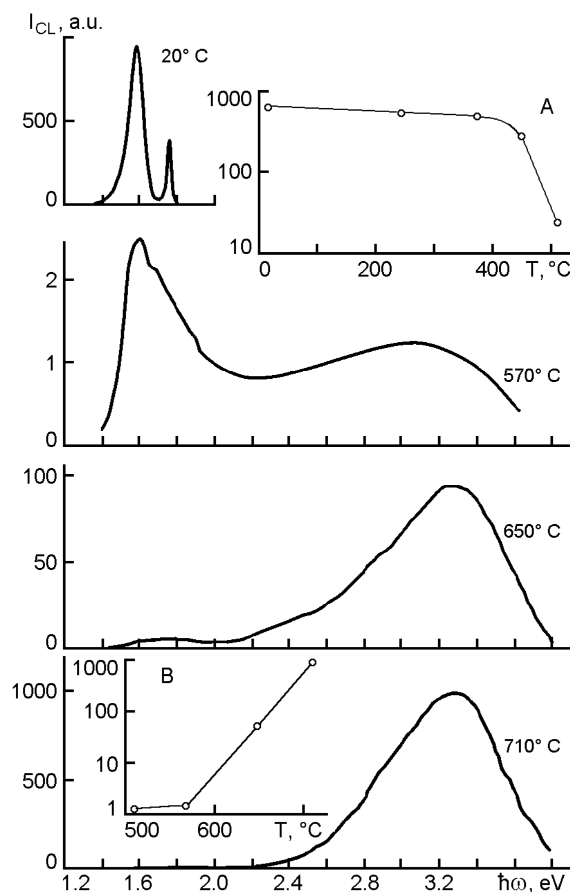

Fig. 1. CL spectra of GaTe single crystals thermally oxidized during 1 h. Temperature dependence of 1.6 eV (*inset A*) and 3.3 eV CL band intensity (*inset B*).

spot diameter on the sample surface 1 mm. Luminescence spectra in the range 1.2–4 eV were recorded using a photomultiplier (FEU-62, FEU-106) through a DMR-4 monochromator.

The luminescence spectra of GaTe single crystals heat treated in air during 1 h are shown in Fig. 1. The CL spectrum of the initial GaTe single crystal consists of two narrow bands which are located in the range of 1.4–1.8 eV. This spectrum differs a little from photoluminescence spectrum of GaTe described in [8], but the last one, as a whole, represents in our opinion the real recombination mechanisms. The band near 1.78 eV is caused by free exciton recombination while the low energy band is related obviously to real crystal structure (presence of structure defects and impurities).

The heating of GaTe crystals up to 400°C does not essentially affect the low energy CL. A slight decrease of its intensity is only observed (Fig. 1, *insert A*). At temperatures over 400°C, the CL spectra are changed drastically. The low-energy luminescence transforms gradually into a broad unstructured band with simultaneous decreasing of the intensity. The temperature elevation from 400 to 550°C is accompanied by a decrease of low energy CL intensity by more than two orders. At the same time, the high-energy luminescence typical of gallium oxide Ga_2O_3 appears in CL spectra (see Fig. 1).

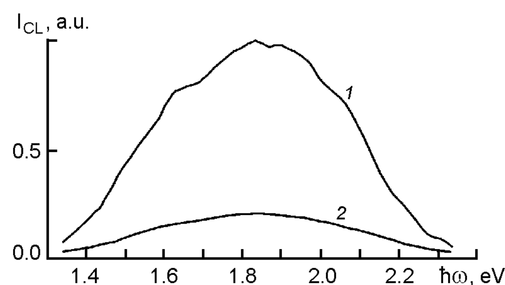

Fig. 2. CL spectra of InTe single crystals thermally oxidized during 1h: *1* — 650°C; *2* — 510°C.

A sharp increase in the CL intensity typical of gallium oxide Ga_2O_3 [9–11] is observed for crystals oxidized at temperatures above 570°C (Fig. 1, *inset B*). Some displacement of the high energy CL maximum with increasing oxidation temperature (see Fig. 1) points out the relative intensity changes of bands forming the high energy CL.

The CL spectra of GaTe crystals oxidized at high temperatures consist also of the band at 1.8 eV (beside inherent β-Ga_2O_3 luminescence). The relative intensity of this band decreases with increasing oxidation temperature (see Fig. 1). Its nature requires a further investigation. However, we can come out with a suggestion based on our previous results on GaSe crystal oxidation [12]. There was also an additional band near 2.0 eV and it was connected with selenium atoms occupying oxygen vacancies in Ga_2O_3 lattice. The oxidized GaS crystals also show an additional CL band near 2.6 eV. In this connection, we could not exclude a similar substitution of oxygen vacancies by tellurium atoms, causing CL emission near 1.8 eV.

Any CL emission of InTe single crystals has not been observed in the range of 1.2–4 eV even after the oxidation at temperatures up to 500°C. The CL appears only after the heat treatment at higher temperatures (Fig. 2). The spectral distribution of such luminescence corresponds to In_2O_3 [13,14]. This means an oxide layer formation. Note that the energy gap of InTe is ~0.8 eV [15], so we did not detect luminescence from the substrate.

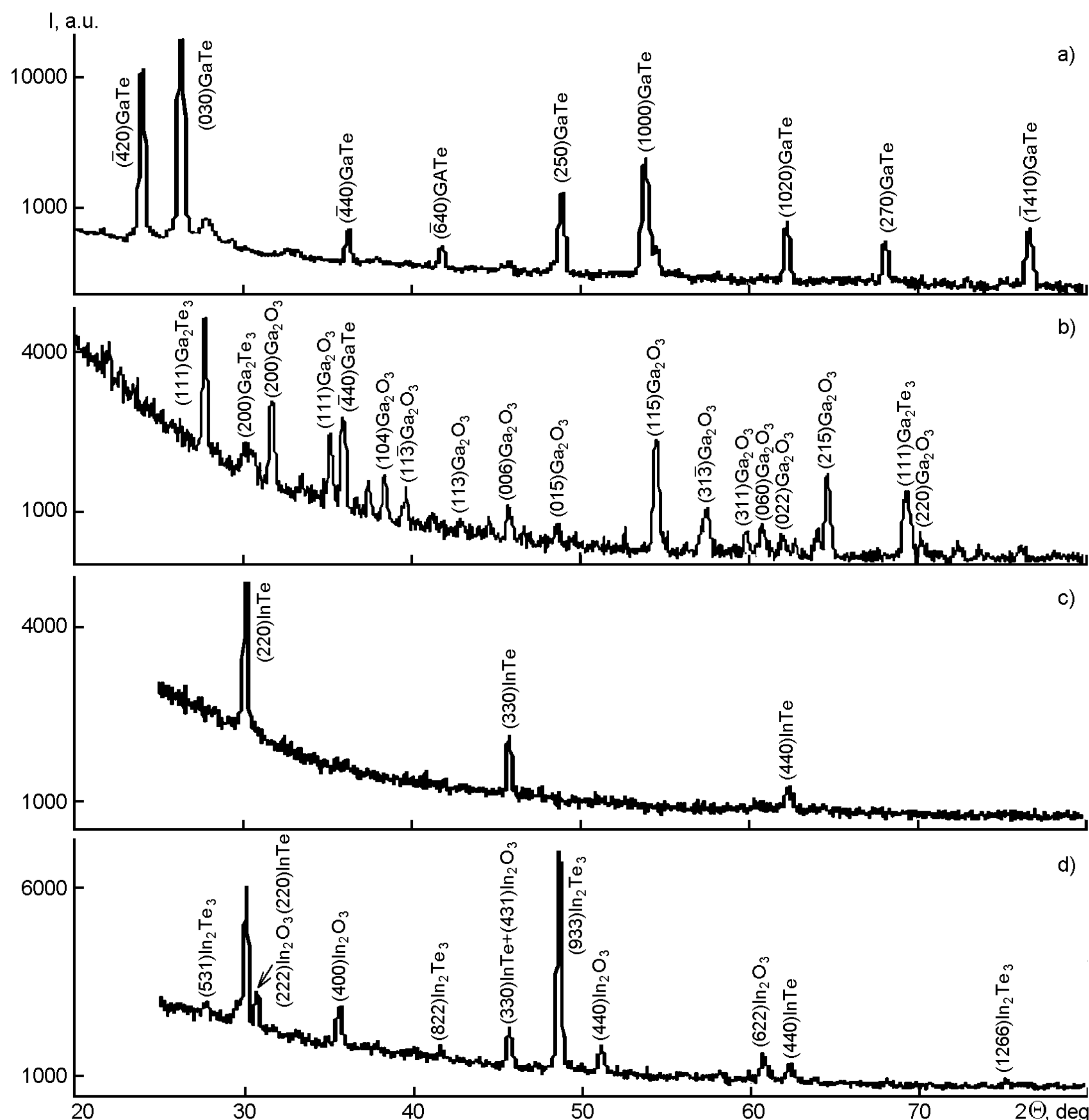

Fig. 3. XRD of thermally oxidized during 3 h at 550 °C (a), 750 °C (b) GaTe and 450 °C (c), 650 °C (d) InTe single crystals.XRD of GaTe and InTe single crystals thermally oxidized during 3 h.

Thus, CL investigations show the temperature development of indium and gallium monotellurides oxidation processes.

The XRD patterns of oxidized GaTe and InTe crystals are shown in Fig. 3. For the sample heat treated at 550°C, only traces of Ga_2Te_3 are observed besides reflexes of the initial compound. At the same time, in the pattern of sample oxidized at 750°C, reflections from the substrate are almost absent and diffraction pattern corresponds to the superposition of Ga_2Te_3 and Ga_2O_3 phases. For InTe, oxidation at temperatures up to 450°C does not change the diffraction pattern, which is characterized by indium monotelluride peaks only. The XRD spectrum of the sample oxidized at 650°C is more complicated. There are reflections from two cubic phases In_2Te_3 and In_2O_3. Neither traces of pure Te, nor its oxide TeO_2 have been detected on XRD patterns of oxidized GaTe and InTe crystals. It is significant that formation of $A_2^{III}B_3^{VI}$ compounds on interface is typical of $A^{II}B^{VI}/A^{III}B^{V}$ compounds (epitaxial growth of corresponding Cd and Zn chalcogenides on the substrates of the indium and gallium arsenides and antimonides [3, 4]). This is justified not only thermodynamically but also by higher (cubic) symmetry of all low temperature modifications of the sesquitellurides of 3rd Group metals.

Table. Calculated tie lines in In–Te–O and Ga–Te–O systems

No.	Reaction equation	ΔG_r^0, kJ·mol^{-1}
1	$8In + 3TeO_2 \rightarrow 2In_2O_3 + In_4Te_3$	−1464.8
2	$4In + 3TeO_2 \rightarrow 2In_2O_3 + 3Te$	−1341.8
3	$In_4Te_3 + 3TeO_2 \rightarrow 2In_2O_3 + 6Te$	−1218.8
4	$2In_2Te_3 + 3TeO_2 \rightarrow 2In_2O_3 + 9Te$	−1133.6
5	$7Ga + 3TeO_2 \rightarrow 2Ga_2O_3 + 3GaTe$	−1096.8
6	$4Ga + 3TeO_2 \rightarrow 2Ga_2O_3 + 3Te$	−805.5
7	$4GaTe + 3TeO_2 \rightarrow 2Ga_2O_3 + 7Te$	−417.0
8	$2Ga_2Te_3 + 3TeO_2 \rightarrow 2Ga_2O_3 + 9Te$	−403.0

Thus, the XRD investigations of oxidized InTe and GaTe crystals supply information additional to CL results. The phases with higher Te contents — In_2Te_3 and Ga_2Te_3, respectively, were revealed by XRD, since their luminescence properties due to narrow band gaps (~1 eV for In_2Te_3 and 0.98 eV for Ga_2Te_3 [3, 15]) do not match to the investigated spectral range.

To analyze the experimental investigations results of the phase transformation consequence during indium and gallium tellurides oxidation, we have considered temperature dependences of equilibrium constants for possible reactions and have constructed the phase equilibrium diagrams.

Consideration of possible oxidation reactions for binary compounds is convenient to perform using phase diagram method [12, 13, 16]. To that aim, interaction between condensed phases in normal conditions is considered. The diagram contains only straight lines joining phase pairs and expressing the thermodynamic equilibrium state between them. The line joining the reaction products with $\Delta G_r^0 < 0$, for all possible intersections with other lines, is considered to be stable. The Gibbs free energy variation of the chemical reaction ΔG_r^0 is determined for intersections points as

$$\Delta G_r^0(reaction) = \sum \Delta G_f^0(products) - \sum \Delta G_f^0(reactants). \quad (1)$$

The normal Gibbs free energy ΔG_r^0 is determined using normal enthalpy ΔH_f^0 of chemical reactions for $T = 298$ K and $p = 10^5$ Pa:

$$\Delta G_T^0 = \Delta H_{298}^0 + \int_{298}^{T} C_p(T)dT - T\left(\Delta S^0 + \int_{298}^{T} \frac{C_p(T)dT}{T}\right), \quad (2)$$

where ΔH_{298}^0 is the formation enthalpy in normal conditions; $C_p(T)$, heat capacity at constant pressure; $\Delta S^0 = S^0{}_{(products)} - \sum S^0{}_{(reactants)}$, the entropy excess. The literature data about the existence of ternary oxides in this system are absent, therefore, we have not included them in the diagram. For other compounds, thermodynamical data can be found in [17–19].

At first, we tested the stability of the lines outgoing from the metal corner of the In–Te–O diagram (*reactions* 1, 2 in the Table). It is seen that the stable lines are In_2O_3–In_4Te_3 and In_2O_3–Te. The last line is also stable for In_4Te_3 and In_2Te_3 with TeO_2 phase reactions (*reactions* 3, 4 in the Table). The lines In_2O_3–InTe, In_2O_3–In_2Te_3 and In_2O_3–In_2Te_5 are stable because of being located between the In_2O_3–In_4Te_3 and In_2O_3–Te stable lines. Similar steps can be made for the Ga–Te–O system. Here, the stable lines are Ga_2O_3–GaTe and Ga_2O_3–Te (reactions 5, 6 in the Table). The last line is also stable for reactions of all semiconductor phases with TeO_2 (*reactions* 7, 8 in the Table). The lines Ga_2O_3–Ga_2Te_3 and Ga_2O_3–Ga_2Te_5 are stable because of being located between the Ga_2O_3–GaTe and Ga_2O_3–Te stable lines. The final Ga–Te–O and In–Te–O phase diagrams are shown in Fig. 4, a.

We have used Gibbs free energy data for corresponding compounds and expressions (1), (2) to calculate the temperature dependences of equilibrium constants. The equations of oxidation reactions have been

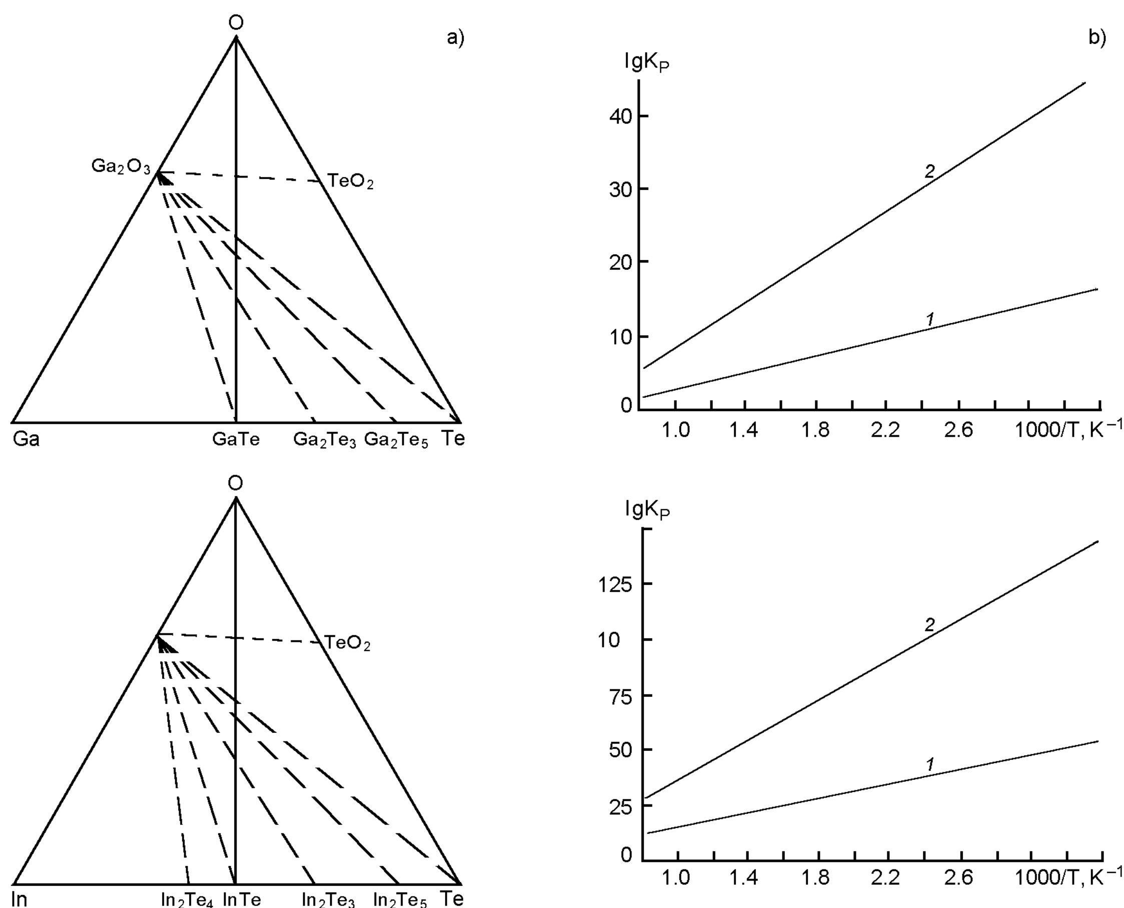

Fig. 4. Phase equilibrium diagrams of Ga–Te–O and In–Te–O systems (a) and temperature dependences of equilibrium constants of gallium and indium monotellurides oxidation reactions (b): *1* — $MeTe + 1/4O_2 = 1/3Me_2Te_3 + 1/6Me_2O_3$; *2* — $MeTe + 3/4O_2 = 1/2Me_2O_3 + Te$.

obtained from the intersection of compound — oxygen line with stable lines of the phase equilibrium diagrams (see Fig. 4, a). We omitted only the reactions with In_2Te_5 and Ga_2Te_5 as products, because there should not be such a amount of free tellurium in the intrinsic oxide film. We also admit that thermodynamically possible reactions with equilibrium constant higher than 1 were considered.

We have determined equilibrium constants for corresponding reactions using the Gibbs free energy (1) and the Van't-Goff isotherm equation:

$$K_p(T) = \exp(-\frac{\Delta G_T^0}{RT}). \quad (3)$$

The calculation results of the temperature dependences of the oxidation reactions of the equilibrium constants for considered compounds are compared in Fig. 4, b. The *reactions* 1 *and* 2 are thermodynamically more efficient for InTe and GaTe compounds. Moreover, the equilibrium constant for *reaction 2* is significantly higher than for *reaction 1* within the whole oxidation temperature range for these compounds (see Fig. 4, b). Therefore, the reaction with gallium oxide formation and elementary Te extraction is dominant. At first sight, such a result is in contradiction with experimental data. However, it must be taken into account that the calculations of equilibrium constants have been performed for equilibrium conditions. But in our case, the diffusion processes such as oxygen diffusion through the surface inside a crystal influence significantly the oxidation reactions. The estimation of oxygen diffusion coefficient in In_2O_3 crystals [20] shows that even at 950°C (significantly higher than our crystal oxidation temperatures), the time needed for relative oxygen concentration to reach 10 % in a depth of 1 μm from the surface, is over 10 h and diffusion time nearly tens of min demands much more

higher temperatures (> 1200°C). Therefore, an obvious lack of oxygen exists inside the crystal that justifies *reaction 1* (per 1 mole of initial compound for *reaction 1*, three times less of oxygen is needed than that for *reaction 2*).

Thus, comparing the experimental results and thermodynamic description of indium and gallium tellurides oxidation processes, the following conclusions can be made. We have established that the oxidation of InTe and GaTe single crystals surfaces involves the formation of phases with a higher tellurium content (In_2Te_3 and Ga_2Te_3), in spite of that corresponding reactions are less favorable than reaction with metal oxide and tellurium as products. Oxidation processes correlate well with thermodynamical analyses only if diffusion features in those crystals are taken into account.

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Фазоутворення у приповерхневих шарах монокристалів GaTe та InTe при термічному окисленні на повітрі

О.О.Балицький, В.П.Савчин, П.В.Савчин, Я.М.Фіяла

Досліджено фазовий склад приповерхневого шару монокристалів GaTe та InTe, термічно оксидованих на повітрі. Встановлено, що оксидування супроводжується утворенням додаткової фази із більшим вмістом телуру — півторателуридів галію та індію відповідно.