Raman study of gallium selenide single crystal oxidation

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Abstract

The Raman investigations on thermally oxidized gallium selenide were conducted. It was established that the oxidation of the GaSe involves the formation of α–modification of Ga_2Se_3 at the temperature up to 450 °C. The $Ga–(O)_2$ complexes are also detected at this temperature but the formation of crystalline gallium oxide takes place at the temperature of 800 °C.

Keywords: III-VI compound, Raman scattering, Phase transformations.

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Introduction

Gallium monoselenide (GaSe) is a promising semiconductor for nonlinear optical applications [1]. Besides GaSe may also be used as a base of semiconductor-own oxide heterostructures for photoelectrical and optical application. The properties of such structures, fabricated by the thermal oxidation have been studied [2,3]. Nevertheless the oxidation processes of gallium selenide is still remaining unclear. X-ray diffraction (XRD) and luminescent properties of thermally oxidised at the 200–450°C GaSe showed, that the own oxide film only contains Ga_2Se_3 [4,5]. At the same time Auger and X-ray photoelectron spectroscopy (XPS) reveals the presence of the gallium oxide [6]. In spite of the difficulties in the obtaining high quality Raman spectra of multicomponent samples [7] this technique is the most sensitive to detect non-crystalline phases during the oxidation processes [8,9]. So in this work we consider the Raman investigation of GaSe single crystals thermal oxidation.

Experimental

The GaSe single crystals, which were not intentionally doped, were grown by Bridgman method. The thermal oxidation was carried out by heat treatment in an electric furnace in the temperature range 450–800 °C. Raman spectra in the range 100–500 cm^{-1} were measured at the room temperature in the backscattering geometry using DFS–24 spectrometer with the exciting light of 488 nm line of an argon-ion (Ar^+) laser.

Results and discussion

Before proceeding to present results, we briefly summarize the previous works, dealing with the GaSe oxidation. In [4] the authors, using the phase equilibria diagram method, showed that oxidation of gallium monoselenide has to be accompanied by the formation of the Ga_2Se_3 phase. XRD of thermally oxidized gallium selenide confirmed this fact (the corresponding XRD peaks are present in the patterns of the samples, thermally oxidized in the temperature

region 450–650°C), but at the same time could not reveal any crystalline oxygen containing phases at the temperatures up to 710 °C [4]. Luminescent properties of such samples, studied in [5], clearly indicate that some wide-gap compound with the intensive luminescent emission at 3.2 eV have been formed during the oxidation at 450–650 °C (the energy gaps of GaSe and Ga_2Se_3 are 2.09 and 1.79 eV respectively). The authors suggested that this emission corresponds to the non-crystalline gallium oxide. The XPS spectrum of the sample, oxidized at 450 °C contains the band, attributed with the binding energy Ga_2O_3, but Ga_2Se_3 is not detected [6]. The authors [6] also pointed out two very important facts: the nonliniar distribution of the oxygen with the depth of samples which may cause the formation of the oxygen rich region in the crystal and the complete absence of any of the Se-O binding at all of the oxidation temperatures. So the additional information, which can be obtained from the Raman investigation, is needed for the explanation of the GaSe single crystal oxidation.

Fig.1a shows the Raman spectrum of the GaSe, heat treated in the air at 450 °C. This spectrum contains 6 intensive bands. Due to work [10] the spectrum of GaSe single crystal is characterised by two intensive Raman peaks: E'' mode at 59±1 cm^{-1} and A_1' at 134±1 cm^{-1}. One can see, that the peak, corresponding to A_1' mode of GaSe is remaining in the spectrum of oxidized at 450 °C sample. All the others peaks in this picture are attributed to the products of the oxidation of GaSe. Thus the peak at 152 cm^{-1} is attributed to the A_1 mode of ordered β–Ga_2Se_3 and the peaks at 246 cm^{-1} and 300.5 cm^{-1} are originated from transverse and longitudinal optical branches of disordered α–Ga_2Se_3 respectively [11]. As the last two are the most intensive we conclude that α–Ga_2Se_3 phase is dominating in the sample.

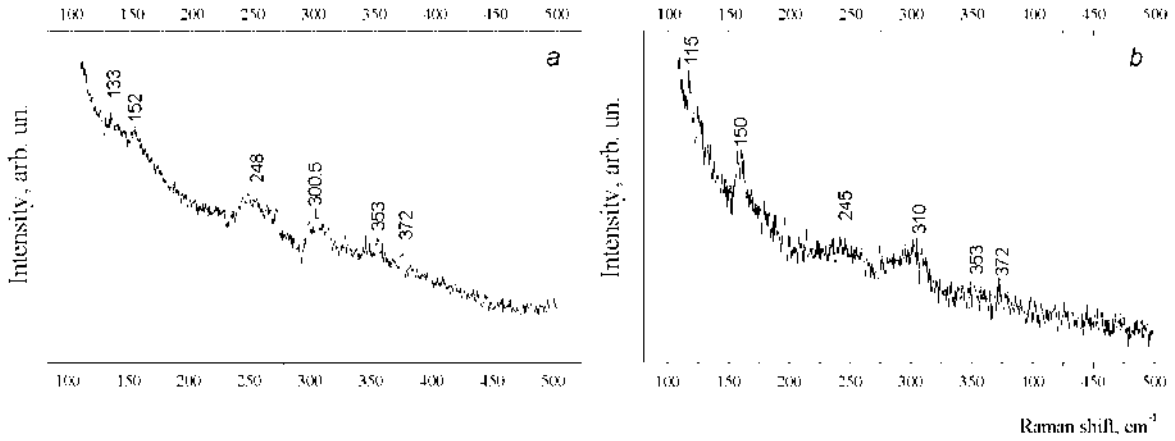

Fig. 1. Raman spectra of GaSe single crystals heat-treated in the air during 1 h at 450°C (a), and 800 °C (b).

As it known the only equilibria phase in Ga-O system is believed to be β–modification of Ga_2O_3 [13]. The precise investigation of Raman and IR modes of β–Ga_2O_3 crystal have been carried out in [14,15]. The authors divided the Raman spectrum of Ga_2O_3 into three spectral regions: the first one (ν<200 cm^{-1}) is related to the lattice modes (vibrations and translation of gallium chains), the second one (200 cm^{-1}<ν<600 cm^{-1}) is assignable to the stretching of the tetraedra complexes Ga–(O_2) and the last one (ν<200 cm^{-1}) corresponds to the bending vibrations of GaO_4 complexes. So using this data we can attribute the bands at 353 and

372 cm^{-1} to the $\perp$ and $\parallel$ rocking of $Ga–(O)_2$ complexes. Note none of the modes, related to the lattice vibration of Ga_2O_3 are observed. The spectrum of the CaSe crystal, thermally oxidized in the air at 800°C is shown in fig.1b. It is easy to see, that numerous bands (310, 345, 150, 115.5 cm^{-1}) have appeared in this spectrum. All of those bands are connected with the translations and librations of gallium atoms, positioned in the Ga_2O_3 monoclinic lattice [15]. None of the modes of gallium selenides are observed. This fact means that we have reached the complete oxidizing of the initial compound.

Conclusions

The mechanism of GaSe oxidation consists of the three stages. At the first one the α–modification of Ga_2Se_3 is formed. Stage two involves the creation of $Ga–(O)_2$ complexes, that are responsible for the formation of the amorphous gallium oxide. The final stage (complete oxidation with the monoclinic $\beta–Ga_2O_3$ formation) takes phase at 800 °C.

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