Structural and optical properties of quasi-2D GaTe layers grown by molecular beam epitaxy on GaAs (001) substrates

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Abstract. Quasi-two-dimensional GaTe layers were grown by molecular beam epitaxy on GaAs (001) substrates at $T_s = 450–520^\circ$C. The effect of the growth temperature on the GaTe surface morphology has been studied by scanning electron microscopy. It is shown that GaTe layer grown at high $T_s = 520^\circ$C exhibits pronounced surface relief anisotropy. This sample demonstrates also near band-edge photoluminescence (PL) at $T = 11 K$ with the peak energy of $\sim 1.72 \text{ eV}$, which can be associated with the emission of excitons bound at the acceptor. The nature of 1.45 eV and 1.57 eV peaks appearing in the PL spectra is also discussed in detail.

1. Introduction

Layered two dimensional (2D) group III metal chalcogenides are still of great interest for the fabrication of new high-performance semiconductor devices due to their unique electronic and optical properties [1,2]. In particular, GaTe as a 2D III-VI material with a direct band gap ($\sim 1.7 \text{ eV}$ at $T = 300 \text{ K}$) is a promising material for creating high-sensitive photodetectors, transistors and solar cells [3-6]. Recently, visible-light photodetectors based on GaTe nanoflakes with photoresponsivities as high as $10^4 \text{ A/W}$ to 532 nm light, which is remarkably higher than that of both graphene and MoS$_2$, have been reported by Liu et al. [3]. Flexible high-performance GaTe photodetectors using GaTe nanoflakes synthesized on mica substrates by chemical vapor deposition (CVD) have been demonstrated by Wang et al. [5].

To date, most 2D layered semiconductors are prepared by mechanical exfoliation from bulk crystals (the Scotch tape technique) and CVD, which limits the possibility of commercial use of these materials for device applications. At the same time, the use of molecular beam epitaxy (MBE) potentially allows fabrication of 2D thin films and heterostructures with uniform wafer-scale film thickness. Moreover, when the epitaxial growth proceeds via van der Waals forces (so-called vdW growth mode), the 2D materials can be grown even on highly-mismatched substrates [7]. The abilities of MBE for the 2D device fabrication have recently been demonstrated by Yuan and co-workers [8], who have fabricated highly efficient photodetector arrays with external quantum efficiency up to 62% and photoresponse time of 22 $\mu$s using few-layer GaTe films grown by MBE on 3-inch Si wafer. The wafer-scale GaTe,Se$_{1-x}$ films grown by MBE on freshly cleaved mica or cleaned silicon substrates were also reported in ref. [9]. However, to the best of our knowledge, there is only one paper devoted to the studies of structural and optical properties of GaTe layers grown by MBE on GaAs (001) substrates [10].
The GaTe is characterized by a very high oxidation rate in air, which leads to a gradual degradation of its optical properties [11]. Therefore, to prevent the atmospheric oxidation of the GaTe, the use of different passivating coatings is required. In particular, the surface passivation with Al₂O₃ was proposed in ref. [11]. The storing of the GaTe samples in vacuum also substantially delays the degradation of optical properties; however this method is not practical for real-life applications.

This paper reports on MBE growth of GaTe layers on GaAs (001) substrates as well as studies of their structural and optical properties.

2. Experiment
GaTe thin films were grown on GaAs (001) substrates with a 200 nm-thick GaAs buffer layer by using a double-chamber MBE setup (SemiTEq, Russia). Standard Ga and Te effusion cells were used as molecular beam sources. The growth temperature \( T_g \) of GaTe layers was as high as \( T_g = 450 \textdegree \text{C} \) (sample \( A \)) and \( T_g = 520 \textdegree \text{C} \) (sample \( B \)), respectively. The Te/Ga flux ratio was controlled by measuring the Te and Ga beam equivalent pressures (BEPs) at the substrate position using a Bayard-Alpert ion gauge. The GaTe growth was initiated by the opening of both Te and Ga shutters on the (2x4) GaAs (001) surface and monitored \textit{in situ} by using reflection high energy electron diffraction (RHEED) technique. The average growth rate \( \langle r_{\text{GaTe}} \rangle \) of GaTe layers were \( r_{\text{GaTe}} \sim 1.3 \text{ nm/min} \) (\( P_{\text{Te}}/P_{\text{Ga}} \) (BEPs) = 10) and \( r_{\text{GaTe}} \sim 1.8 \text{ nm/min} \) (\( P_{\text{Te}}/P_{\text{Ga}} \) (BEPs) = 16) for the samples \( A \) and \( B \), respectively. The Te/Ga flux ratios were chosen to provide the Te-rich conditions in accordance with Bae et al. [10]. The samples were characterized by scanning electron microscopy (SEM) (CamScan microscope) and low-temperature photoluminescence (PL) spectroscopy (\( \lambda_{\text{exc}} = 405 \text{ nm} \)) techniques.

3. Results and discussion
The MBE growth of different layered III-VI's (e.g., InSe or GaSe) is characterized by several common features. First of all, one of the main problems is the formation of numerous “parasitic” phases, i.e., In₃/Se₃ and In₂Se₅ [12] or Ga₂Se₃ [13,14] at MBE growth of InSe and GaSe, respectively. In case of GaTe the possible phase is Ga₂Te₃ [15]. It should be noted, that Ga₂Te₃ films were successfully synthesized by metalorganic MBE on both InP (001) and GaAs (001) substrates at \( T_s = 400-500 \textdegree \text{C} \) under strong Te-rich conditions (Te/Ga ~ 30) [16,17]; however, no evidence of Ga₂Te₃ inclusions have been obtained at MBE growth of GaTe/GaAs (001) at much lower (Te/Ga ~ 10) flux ratio [10].

Another problem in MBE of layered III-VI’s is the existence of a large number of polytypes. The GaTe layers are ~0.8 nm in thickness [6,8] and preferentially stack in the monoclinic \( \alpha \)-structure (m-GaTe), which is more stable than hexagonal close-packed \( \beta \)-structure (h-GaTe) [10,18,19]. In particular, the thickness-dependent transformation of hexagonal h-GaTe to the monoclinic m-GaTe structure at MBE growth of GaTe on GaAs (001) substrates have been observed in ref. [10]. At substrate temperature \( T_s = 450 \textdegree \text{C} \) and Te/Ga(BEP) = 10 the critical thickness of h-GaTe to m-GaTe transformation has been estimated as high as ~90 nm. Considering, that the driving force of the transition is a decrease in free energy [19], we can suppose that the growth temperature should definitely affect the critical thickness of this transformation.

The growth temperature is the main factor affecting the properties of the III-VI layers. Generally, the layers grown at higher \( T_s \) demonstrate the better crystal and optical quality. The plan-view SEM images of the samples \( A \) and \( B \) grown at different \( T_s \) are presented in figure 1. The surface morphology of sample \( A \) (figure 1a) is typical for the MBE grown III-VI’s. For example, a similar surface morphology was observed for the GaSe layers grown by MBE at low \( T_s \approx 400 \textdegree \text{C} \) [13]. One can see a number of so-called “nanoplatelets” of different sizes and shapes randomly distributed on the relatively flat growth surface. In contrast, the plan-view SEM image of sample \( B \) (figure 1b) exhibits pronounced surface relief anisotropy, which can either be related to the strong anisotropic nature of the m-GaTe crystal structure, or it can be induced by the large lattice mismatch between the GaTe and GaAs (001) substrate [20].
Figure 1. Plan-view SEM images of the GaTe layers grown on GaAs (001) substrates at different substrate temperature: (a) sample $A$, $T_S = 450°C$, (b) sample $B$, $T_S = 520°C$. The insets show cross-section SEM images of the respective structures.

An increase in the growth temperature can lead to chemical interaction between the substrate and the growing layer, and the van der Waals mode is not realized. This interaction in case of GaSe/GaAs (001) MBE growth ($T_S > 500°C$) results in the significant surface morphology transformation because of the growth of inclined nanoplatelets [21]. However, the cross-section SEM image of sample $B$ (see inset in the figure 1b) grown at $T_S = 520°C$ demonstrates the formation of a relatively plain layer with nearly abrupt GaTe/GaAs (001) interface.

Figure 2. The evolution of the RHEED patterns along the $[\overline{1}1\overline{2}0]$ direction at the MBE of GaTe/GaAs (001) grown at low $T_S = 450°C$ (sample $A$): (a) the layer thickness of $\sim 4$ nm; (b) the layer thickness of $\sim 9$ nm. (c) The RHEED pattern of sample $B$ grown at $T_S = 520°C$ (the layer thickness is $\sim 30$ nm).

The RHEED images during the growth of samples $A$ and $B$ are presented in figure 2. One can see the RHEED pattern remains streaky for both samples. However, the reflexes are thickened and blurred for the sample $A$ grown at low temperature ($T_S = 450°C$) (figure 1(a,b)), and the brightness of the
RHEED pattern gradually decreases with increasing layer thickness. This behavior reflects an increase in surface roughness as the layer grows, and can be induced by the formation of multi-domain structure at initial growth stage, i.e., the MBE growth of GaTe is similar to that observed for GaSe/GaAs (001) at low substrate temperatures [13]. In contrast, the RHEED image of sample B \((T_s = 520^\circC)\) demonstrates more narrow reflexes (figure 2c), confirming that the higher the growth temperature, the higher the crystal quality of the growing film.

![Figure 3](image-url)

**Figure 3.** (a) GaTe/GaAs PL spectrum of sample B after the 19 days storage in vacuum. (b) The dependence of the intensity of PL peaks for the sample B on the storage time in a closed-cycle helium cryostat. The PL intensity is normalized to the PL peak with energy of 1.25 eV.

To understand the difference between samples A and B we have performed PL measurements. The as-grown samples were transferred through the air from the MBE load lock into a closed-cycle helium cryostat, after that they were stored in vacuum at room temperature for three weeks (more precisely, 19 days). Then the samples were exposed in air for 24 hours and again continued to be stored in vacuum. The PL spectra were measured at \(T = 11K\) in a closed-cycle helium cryostat using a laser source with the excitation wavelength of \(\lambda_{exc} = 405\) nm. The laser power on the sample was as low as 50 mW with a spot of \(-0.1\) cm\(^2\), which corresponds to the excitation power density of 0.5 W/cm\(^2\). PL spectrum of sample B, measured on the 19\(^{th}\) day of storage in vacuum, is presented in figure 3a. The shortest wavelength peak located at \(-1.72\) eV could be associated with the emission of acceptor-bound excitons [22], while the broad band centered at \(1.57\) eV is presumably associated with donor-acceptor pair (DAP) recombination [23,24]. This interpretation is in good agreement with the assumption that Te-rich growth conditions should cause the layer to exhibit \(p\)-type natural conductivity [10]. One of the possible explanations of \(1.45\) eV peak is that it originates from the GaAs substrate. However, this peak was not observed in the PL spectrum of sample A, and the PL maximum is shifted by \(-50\) meV toward a longer wavelength compared to the peak from the GaAs substrate. It is also highly unlikely that this peak is due to radiation from the hexagonal h-GaTe. Although the weak broad PL emission at \(1.44\) eV \((T = 300K)\) was observed by Fonseca et al. [24] from the hexagonal GaSe\(_x\)Te\(_{1-x}\) islands with low Se content \((x \leq 0.05)\), according to [25] the hexagonal GaTe should possess bandgap at \(1.03\) eV, which does not correlate with intense emission at \(1.45\) eV. Moreover, the X-ray diffraction (XRD) spectrum of sample B (not shown here) indicates the dominance of monoclinic GaTe [10,19]. Following the Cai et al. [20], we can suppose that this peak can be associated with the emission centers localized at the domain edges. The dominance of this defect emission (1.45 eV) in the spectrum can be explained by much lower power density of the excitation laser in our measurements in comparison with that used by Cai et al. [20]. The absence of this peak in the sample A grown at \(T_s = 450^\circC\) can be associated with much worse structural perfection of layer A compared to B. The peak at \(1.25\) eV, which is the only one registered in the PL spectra of both samples \((A\) and \(B)\),
probably corresponds to the radiation of a gallium vacancy complex in the GaAs substrate [27]. This assumption was confirmed by observation of the same peak in the PL spectrum of the bare GaAs substrate without the GaTe layer. Nevertheless, this peak can also be related to the defect emission in GaTe, since the PL intensity at 1.25 eV in sample B is by an order of magnitude higher.

Recently, Fonseca et al. demonstrated that GaTe exposure to air produces significant conduction band restructuring due to the incorporation and chemisorption of oxygen to tellurium, forming the GaTe–O2 phase [26]. Given that the transformation occurs with at least the presence of oxygen in air and it’s facilitated by surface defects, the rate of transformation could be controlled by adjusting the ambient conditions, e.g. by storing samples in vacuum. Figure 3(b) presents the dependence of the integral intensity of PL peaks located at 1.72 and 1.57 eV for sample B versus the storage time in the closed-cycle helium cryostat. The PL intensity has been normalized to the PL peak with energy of 1.25 eV. The gradual increase of the near band-edge PL intensity (1.72 eV peak) on storage time could be explained in different ways, e.g. by the annealing of the defects under laser irradiation. It is also possible that the increase in PL intensity is associated with the release of molecular oxygen adsorbed on GaTe during sample transfer from the MBE load lock to the cryostat.

Anyway, after the secondary exposure of the sample to air, the PL intensity decreases because of oxidation [11]. The oxidation of GaTe was also confirmed by the transformation of XRD pattern (not shown here) of GaTe layer stored in ambient conditions.

4. Conclusions

The structural and optical properties of GaTe thin films grown by MBE on GaAs (001) substrates have been studied using SEM and PL techniques. It is found that the surface morphology of the GaTe layer grown at $T_5$ = 520°C exhibits pronounced anisotropy. The GaTe layer grown at high $T_5$ = 520°C demonstrates near band-edge PL at T = 11K. The peak with energy of ~1.72 eV is associated with the emission of excitons bound at the acceptor in GaTe, which is in a good agreement with strong Te-rich conditions used at MBE growth. The time dependence of the PL intensity of GaTe layer confirms the necessity of storing the samples in vacuum to avoid the atmospheric oxidation of GaTe.

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