Heteroepitaxy of InSe/GaSe on Si(111) Substrates

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Abstract

High quality growth of InSe on Si(111) was achived by insertion of GaSe buffer. Rombohedral polytepes were formed in both, the InSe and GaSe layers. Twining and stacking disorder was often detected in these materials due to they layered structure. Moreover, in samples with thin GaSe layer, a strong interdiffusion of indium into the GaSe layer was detected which resulted in the formation of In_xGa_ySe phase. The dominant threading defects present in these InSe/GaSe heterostructures were screw dislocations, which seem to act as nonradiative recombination centers.

Introduction

Due to its favorable structural and electrical properties, InSe is a candidate for application in novel high density storage medium [1]. Such silicon-process-compatible medium device based on epitaxial InSe/GaSe heterojunction diode has been constructed recently and current gain of 65 has been demonstrated at 2 keV electron beam energy [2]. Here in this paper we investigated structural properties of such InSe/GaSe heterostructures grown on S(111) substrates.

Both, InSe and GaSe are layered III-VI compounds stacked of identical sheets which are composed of four atomic layers – two layers of group III (either Ga or In) sandwiched between two layers of Se. Each group III atom is bound through ionocovalent bonds with three, equally distant, neighboring Se atoms and with the equivalent group III atom from the next group III layer. There are no dangling bonds in this system therefore such sheets are bonded together only through weak van der Waals-like interactions. Different polytypes of these layered materials can be formed depending on sheets stacking sequence. In case of InSe and GaSe there are two most commonly observed polytypes: (1) hexagonal ε-polytype (space group $P6_3/mmc$) with a stacking sequence described by ABAB…and (2) rhombohedral γ-polytype (space group *R3m*) with a stacking sequence described by ABCABC…. Unit

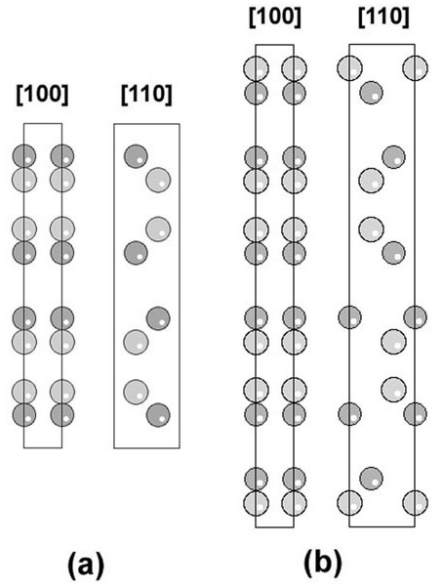

Figure 1. Unit cells of a hexagonal (a) and a rhombohedral (b) polytype of GaSe.

cells of these GaSe polytypes, projected along [100] and [110] direction, are show schematically in Fig. 1.

Experimental details

Si wafers, both, with exact (111) orientation and having 4 deg of miscut were used as substrates for the InSe/GaSe growth. They were cleaned prior the growth using a buffered-oxide etch or an ethanol/HF mixture. The GaSe growth was conducted at ~550°C. Temperature was then reduced to ~450°C and InSe layer was grown on top of the GaSe film. Both films were grown from elemental Knudsen-cell. Several sets of samples with thickness of the GaSe layer ranging from 5-10 nm to 200-300 nm and with that of the InSe film from 30-50 nm to ~500 nm were grown for this study.

All films were first characterized using four-circle x-ray diffraction in order to confirm their epitaxial layered structure. Then they were studied using transmission electron microscopy (TEM). TEM sample preparation was a challenging task as GaSe films were very weakly bonded to Si substrates. In order to prepare cross-sectional TEM specimen for each sample two rectangular pieces, rotated by 90° (in order to study two main crystallographic orientations), were glued together with their InSe/GaSe layers facing each other. Such specimen was then mechanically grinned and polished to a thickness of about 10 μm and finally Ar-ion milled to electron transparency. Unfortunately, often during such process the whole InSe/GaSe layer delaminated from the Si substrate and was damaged during ion milling. This precluded TEM study of one and for some samples even both orientations.

Different TEM techniques including selected area electron diffraction (SAED), diffraction contrast analysis and high resolution electron microscopy (HREM) were used to study these InSe/GaSe/Si(111) samples. Energy-dispersive x-ray analysis (EDX) was also performed for most of them.

Results and discussion

TEM studies showed a good layered structure of our InSe/GaSe films grown on Si(111) substrates. They had uniform thickness and relatively flat surfaces indicating that a two-dimensional growth mode was obtained. An example of bright field TEM of a typical sample is shown in Fig. 2a. TEM observations were consistent with x-ray diffraction results, which confirmed the epitaxial structure of the InSe and GaSe films. Fig. 2b shows x-ray diffraction pattern from a typical InSe/GaSe/Si(111) sample. In addition to $(111)_{Si}$ peak at $2\theta \sim 28.3^o$ there are two sets of peaks visible in this pattern. First with a spacing between subsequent peaks of ~10.65^o (equivalent of ~8.30 Å in a d-spacing) originates from the InSe film and the second one with a spacing between peaks of ~11.15^o (equivalent of ~7.90 Å in a d-spacing) originates from the GaSe film. Weaker additional peaks were also sometimes observed indicating the presence of secondary phases, which were identified either as In_4Se_3 or γ-In_2Se_3. Based on x-ray diffraction it was difficult to distinguish between hexagonal and rhombohedral polytypes of InSe (GaSe) since they differ only slightly in d-spacing. Therefore, we used symmetry of SAED patterns. Figure 2c shows a section of SAED pattern obtained from a typical InSe/GaSe/Si(111) sample. It contains bright spots originating from the GaSe layer and weaker ones, located slightly closer to the (000) beam, from the InSe layer. Below are shown patterns, covering the same region of the reciprocal space, simulated for the rhombohedral (Fig 2d) and the hexagonal (Fig 2e) GaSe. Comparison

between these simulations and experimental pattern indicates that the rhombohedral polytype dominates in our GaSe films. The same is true for InSe as symmetry of the diffraction pattern remains the same.

Both, the x-ray diffraction and SAED results, indicate that for layers grown on Si(111) substrates with exact orientation the orientation relationship between Si and GaSe is described as follows: $[001]_{GaSe} \parallel [111]_{Si}$ and $[1\underline{2}0]_{Se} \parallel [1\underline{1}0]_{Si}$. For layers grown on 4° miscut substrates the $[001]_{GaSe}$ deviates from the $[111]_{Si}$ by 4°. It is interesting however, that the $[1\underline{2}0]_{Se}$ direction also deviates from $[1\underline{1}0]_{Si}$ by the same angle and there is approximately the same orientation relationship as in the case of exactly oriented substrates. For all samples the orientation of InSe follows that of the GaSe film.

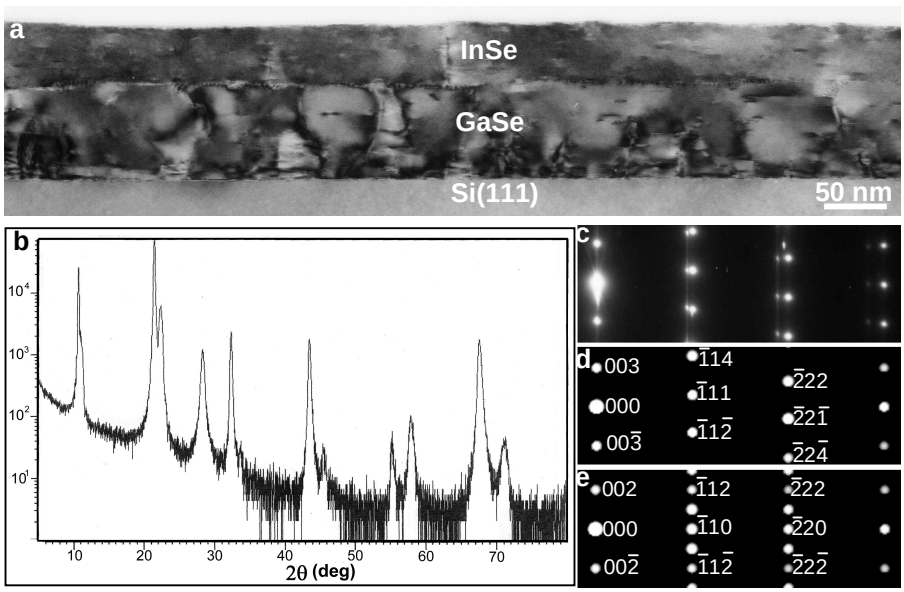

Figure 2. (a) X-ray diffraction pattern (a) and SAED pattern (b) from a typical InSe/GaSe/Si(111) sample. SAED patterns from the same region of the reciprocal space as this shown in (a) simulated for rhombohedral (c) and hexagonal (d) GaSe polytype.

For many samples it was observed, that [110] SAED pattern (similar to this shown in Fig. 2c) contained a regular set of extra spots. An example of such patterns is shown in Fig. 3a. In this pattern each GaSe diffraction spot of a (1-1l)- or (2-2l)-type is accompanied by an additional spot located at 1/3 of a distance to the next spot from this row (additional spots are indicated by circles). On the other hand, (00l)- and (3-3l)-type spots have no such neighboring additional spots. The same behavior is visible for weaker InSe spots. This can be described more generally as follows. All primary GaSe (InSe) primary reflections can be divided into three groups: (1) (h_1,-h_1, 3m+1), (2) (h_2,-h_2, 3m+2) and (3) (h_3,-h_3, 3m), where h_1= 3n+1, h_2= 3n+2, h_3= 3n and m,n = 0, ±1, ±2,… .Each group corresponds to every third row of spots. Additional reflections can be described in similar manner: (h_1,-h_1, 3m+2) and (h_2,-h_2, 3m+1). It can be noticed that additional reflections can be obtained from primary reflections by symmetry operation ρ, which is a mirror reflection with a mirror plane containing (000) and (h,-h,0) reflections: ρ(h_1,-h_1, 3m+1) = (h_1,-h_1, 3m^*+2) and ρ(h_2,-h_2, 3m+2) = (h_2,-h_2, 3m^*+1), where m^* = 0, ±1, ±2,… . On the other hand, the same symmetry operation applied to the primary reflection of the third group produces a reflection, which also belongs to the third group of primary reflections: ρ(h_1,-h_1, 3m) = (h_1,-h_1, 3$m^\#$), where $m^\#$ = 0, ±1, ±2,… . This explains a lack of additional spots associated with reflections of group third in experimental diffraction pattern. Summarizing, GaSe (InSe)

diffraction pattern shown in Fig. 3a is a superposition of a regular rhombohedral pattern and such a pattern transformed via the symmetry operation ρ. In real space this symmetry operation corresponds to a mirror reflection with a mirror plane at a c-plane, which means that GaSe (InSe) layer contains sublayers with two opposite "polarities" described by following stacking sequences: (1) ABCABC… and (2) CBACBA… . When two such layers are located next to each other a twining occurs (described by the stacking sequence: …ABCABCBACBA…) and there is a stacking fault on a c-plane associated with it. The presence of such stacking faults is revealed by the striking (smearing) of diffraction reflections along the c-direction in Fig. 3a. A TEM image of the same sample, viewed along the [110] projection, shows high density of horizontal planar, which separates twinned regions. Among samples, which were used for this study, there were samples with different relative intensity of primary and twinning spots. There were samples without twinning spots like this shown in Fig. 2c, samples with such weak spots and samples such as this shown in Fig. 3a where twinning spots had comparable intensity to that of primary spots. This suggests that different degree of twinning was present in these samples however, no evident correlation between this degree and growing parameters or other characteristics of these layers was observed.

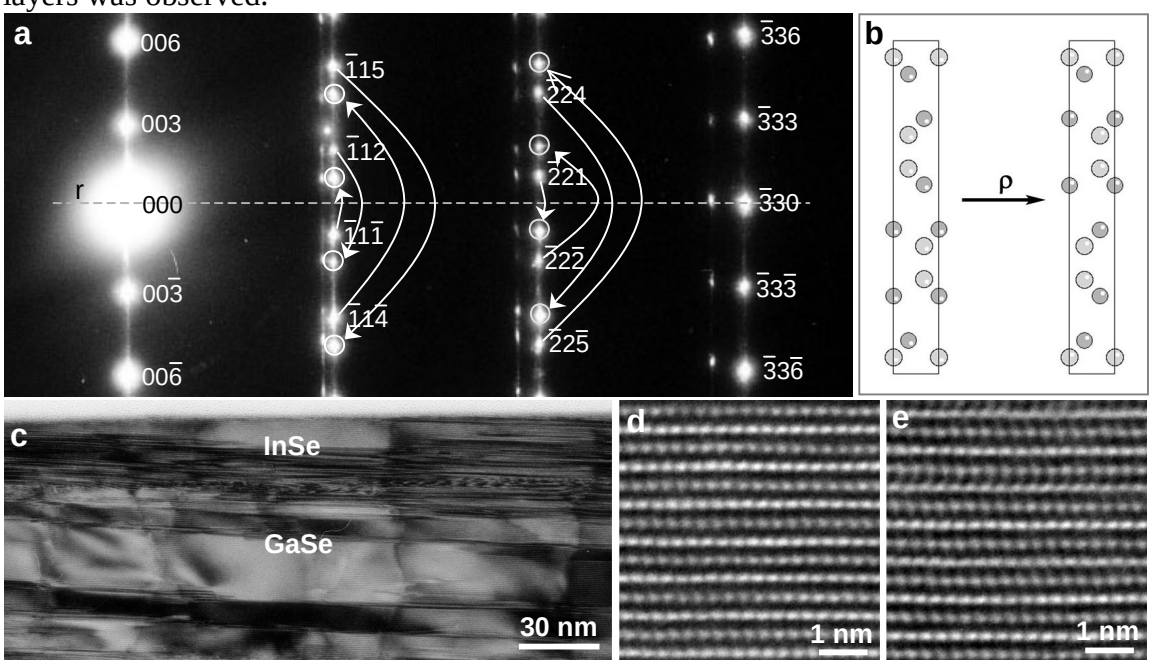

Figure 3. (a) [110] SAED pattern of InSe/GaSe/Si(111) sample with high density of twinning in both GaSe (strong spots) and InSe (weaker spots located closer to the (000) beam). Twin GaSe spots are indicated by white circles. A dashed line shows the plane of the mirror symmetry ρ of this pattern. White arrows indicate from which primary reflection the particular twinn reflection was formed. (b) A schematic representation of such mirror symmetry (twinning) in a real space. (c) TEM image of taken from the InSe/GaSe region of the same sample. Notice high density of twins separated by horizontal defects. (d) and (e) HREM [110] image of perfect and disordered GaSe regions.

In addition to twinning there are two other types of structural defects present in these layers. First of all, in many samples TEM revealed substantial degree of stacking disorder. Basal stacking faults are associated with it. Figs 3d and 3e shows respectively high resolution electron microscopy (HREM) images of a perfect GaSe region and GaSe region with such a stacking disorder. The second type of structural defects are threading dislocations. Diffraction contrast experiments show that they are in good contrast for g-vector parallel to the c-axis (Fig. 4a) and

are out of contrast for g-vector perpendicular to the c-axis (Fig. 4b). It suggests then that these dislocations have burgers vector parallel to the c-axis and are screw-type since their lines are also predominantly along the c-direction. The density of dislocations in the GaSe layer is relatively high (~10^{11} cm^{-2}). They nucleate at the GaSe/Si interface and propagate to the InSe/GaSe interface where majority of them combine and form halfloops (see Fig. 4a). As a result only few dislocations re-emerge in the InSe (~10^{10} cm^{-2}) and propagate to the surface. It is know from other materials that threading dislocations can act as nonradiate recombination defects and can limit minority carriers lifetime and their diffusion length [3]. It seems that threading dislocations can play similar role in InSe layers as minority carriers diffusion length of 0.2 μm, reported for InSe [4], correlates well with the average separation between dislocations which can be deduced from dislocation density measured in our layers (~0.1 μm).

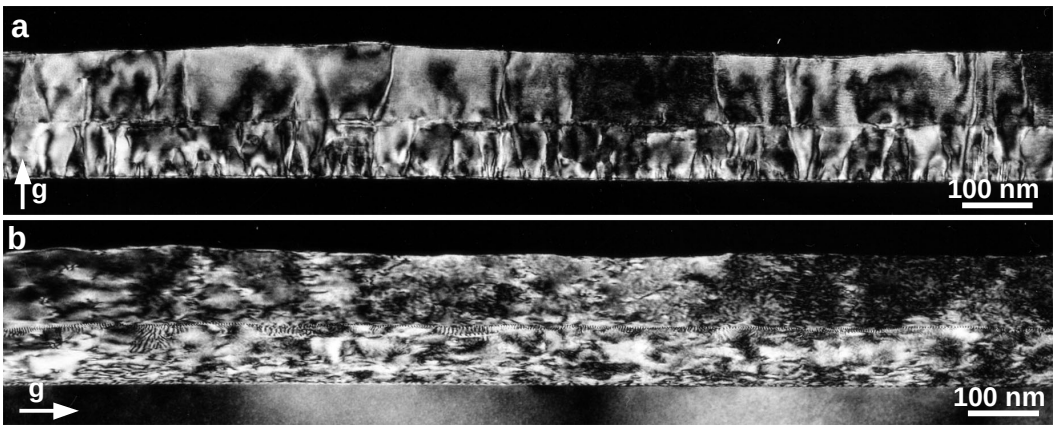

Figure 4. Dark-field images of InSe/GaSe/Si(111) sample taken with g-vector: (a) parallel and (b) perpendicuar to the c-axis. Notice high density of dislocations in (a). They are out of contrast in (b).

EDX measurements showed that in many samples, especially in these with thin GaSe layer, a strong interdiffusion occurs at the InSe/GaSe interface. This is can be seen in Fig. 5a which shows EDX line profiles across the layer structure in one of such samples. One can see from this data that there is very high concentration of indium in the GaSe layers. Similar results were found for many other samples. Also SAED suggests a strong In interdiffusion in samples with thin GaSe layers. Fig. 5b presents lattice parameters determined from SAED which were measured for GaSe and InSe layers in different samples. Values relative to these reported for bulk materials are shown in this Figure. They are plot as a function of a thickness of the GaSe layer. One can see from this data that for all samples lattice parameters of InSe agrees within the experimental errors with bulk values. The same is true for GaSe as long as thick they are relatively thick. However, For thin GaSe layers (10-25 nm) a significant increase in both, c- and a-lattice parameters, is detected. This suggests that the In_xGa_ySe layer with high concentration of In is formed instead of pure GaSe. The mechanism of such interdiffusion is not yet clear however, similar phenomenon has already been reported in the case of InSe/GaSe/GaAs(100) epitaxy [ref].

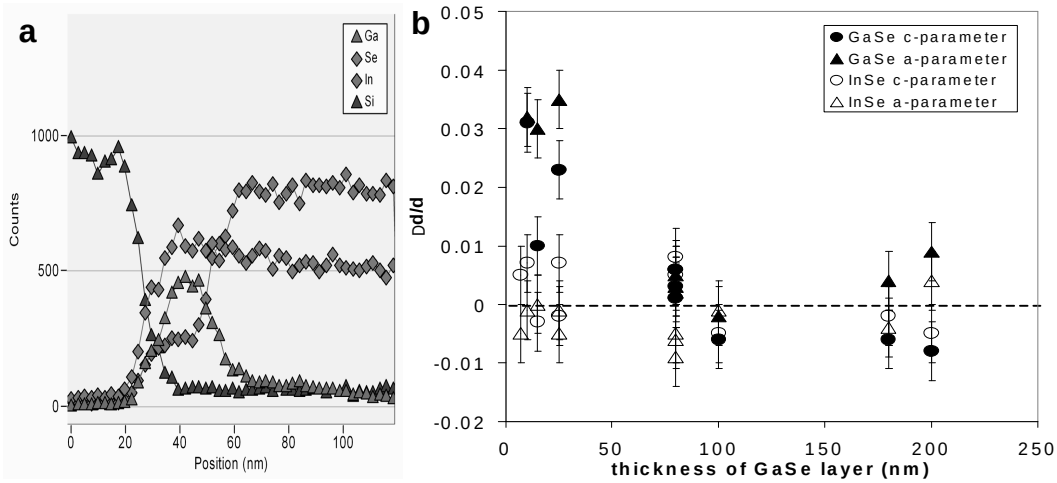

Figure 5. (a) EDX line profiles measured across layer structure in sample with thin GaSe layer. (b) Lattice parameters of GaSe and InSe layers determined from SAED. This plot presents data from several samples as a function of a thickness of the GaSe layer. Notice increased lattice parameters for thin GaSe layers.

Conclusions

In summary, both TEM and x-ray diffraction, indicate good structural quality of InSe/GaSe heterostructures grown Si(111) substrates. These layers crystallize in form of rombohedral polytypes, they have uniform thickness and relatively flat surfaces. A good quality of InSe/GaSe/Si(111) heterostructures seem to be consistent with the work of Budiman et al. [5] which shows that direct growth of InSe on GaAs(100) is very difficult, whereas an insertion of a GaSe layer leads to much better quality of InSe film. The GaSe intermediate layer seems to play a similar role in the case of Si(111) substrates, e.g. passivates the substrate dangling bonds [6]. Both InSe and GaSe are layered materials and it was found that twining and stacking disorder can be easily introduced during the growth. Screw dislocations seem to be dominant threading defects and they are probably responsible for short diffusion length of minority carriers in InSe. Our study shows also that in samples with thin GaSe layers strong interdifussion of In occurs leading to the formation of In_xGa_ySe phase.

Acknowledgments

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