## Atomic-Layer Epitaxy of ZnSe and ZnTe Single Crystalline Films and its Application to the Fabrication of ZnSe/ZnTe Superlattices

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Single-crystalline films of ZnSe and ZnTe have been grown for the first time by ALE. The initial and successive stage of the epitaxy has been elucidated by using electron diffraction techniique. Feasibility of fabricating ZnTe/ZnSe superlattice by ALE has been shown.

## 1. Introduction

Recently, atomic layer epitaxy (ALE) growth of II-VI compound semiconductros has attracted considerable attention<sup>(1)</sup>. In this technique complementary role of the constituent elements is essential in the growth mechanism, as well as MBE of II-VI compounds. In fact, the first experimental verification of the fact that the constituent elements play a complementary role to each other in the epitaxial growth process has been given by the detailed investigation of the growth rate against the molecular beam intensities in MBE growth<sup>(2)</sup>. This is because the elements of the groups II and VI are much more volatile than their compounds, excess incident molecular beams impinging the film will reevaporate immediately at the properly fixed substrate temperature. On the basis of this experimental findings, ALE of II-VI compounds have been carried out<sup>(1)</sup>.

In the case of ALE, monolayers of constituent elements are alternately deposited onto the substrate under ultra high vacuum conditions as molecular beams from Knudsen cells. It has been believed that the film growth occurs stepwise at relatively low substrate temperature<sup>(1)</sup>. No accurate control in turning the molecular beams on and off is required. The film thickness is determined by the total number of opening and closing cycles of the sources rather than by the beam intensity or source temperatures, provided that at least one complete coverage of a constituent element is formed on the substrate before the next molucular beams are allowed to react with the surface. On account of these important features of ALE, precise control of film thickness in atomic layer scale is attainable, which will be of great advantage when fabricating superlattice structures of Zn-chalcogenides.

So far, ALE growth of Zn-chalcogenide films have been concerned only with polycrystalline films on glass substrates, intending their application to electroluminescent devices. Although it has been believed that the film growth occurs atomic-layer by layer, the growth mechanisms of ALE has not yet been investigated.

The purposes of this paper are to to elucidate the initial and successive stage of the epitaxy, to establish the growth technique of single-crystalline films of Zn-chalcogenides by ALE, and to try to fabricate ZnSe/ZnTe superlattice structure by ALE.

## 2. Atomic layer epitaxy

We have grown ZnSe and ZnTe on (001)GaAs substrate. Before commencing growth, the substrate was thermally cleaned at  $630^{\circ}$ C for lmin. The substrate temperature during growth was in the range  $200-400^{\circ}$ C for ZnTe and fixed at  $280^{\circ}$ C for ZnSe.

A typical deposition sequence of Zn and Te for ALE growth of ZnTe is shown in Fig. 1. Zn and Te were alternately deposited onto the substrate as molecular beam pulses of Zn and Te<sub>2</sub>



Fig. 1. A typical deposition sequence of Zn and Te for ALE growth of ZnTe.

Fig. 2. ZnTe and ZnSe film thickness against total number of turning on and off cycles of the molecular beam sources.



produced from separate sources. Typical source temperatures were 320, 160, and 330°C for Zn, Se, During one complete cycle and Te, respectively. of opening and closing a shutter, the substrate was exposed to the molecular beam pulse to produce a coverage thicker than two monolayers if we assumed that no re-evaporation of the elements had However, ALE growth must be carried occurred. out at a substrate temperature where excess atoms that do not form II-VI bonds in the film are reevaporated. Between the two successive pulses, all beams were turned off for one or two seconds. Accordingly, a thermal equilibrium of the surface was approached at the end of each growth step.

Figure 2 shows the film thickness against the total number of opening and closing cycles of the shutters. The solid line shows a calculation under the assumption that an average layer thickness obtained per cycle is the thickness of one monolayer, a/2 for (001)ZnSe and ZnTe, where a is the lattice constant. It is clearly shown that one atomic layer is grown for one cycle of opening and closing of the constituent elements.

## 3. RHEED observation

The surface crystallinity of epilayers has been examined "in situ" using RHEED at 20keV. The deffraction pattern with the electron beam along the [110] azimuth is shown in Fig.3. After thermally cleaned, the substrate was cooled down to 230°C which is extremely low compared with MBE whose substrate temperature is typically 300-400°C. The corresponding RHEED pattern showed only bulk spots, with no reconstruction and slight streaking indicating that surface was rather rough on an atomic scale (Fig.3(a)). Figures 3(b), (c), and (d) show the diffraction patterns from Zn-covered surface after depositing film thickness of 10, 50, and 200 monolayers, respectively. When 10 monolayers of ZnTe are deposited, the surface shows much rougher surface as observed by spotty RHEED pattern together with excess streaks which is indicative of facet growth (Fig.3(b)). When 50 monolayers are deposited, the RHEED pattern shows elongated spots suggesting the overgrowth surface is decreasing in roughness in comparison with the original GaAs surface The deposition of 200 monolayers (Fig.3(c)). improve the surface morphology as indicated by the streaky RHEED pattern (Fig.3(d)). The deposition of 2000 monolayers generated a strongly streaked pattern with little intensity modulation along the length of the reciprocal lattice rods, indicating smoothness on atomic scale.

The observed evolution of RHEED patterns will be understood as follows: After the deposition of more than several monolayers, three dimensional growth mechanism dominates. However, as the deposition procedes more than 100 monolayers, the film becomes smooth, presumably because of the coalescence of islands on the surface. Eventually, pseudo two-dimensional growth mechanism takes place. Similar evolution of the RHEED pattern was observed in ALE growth of ZnSe on (001)GaAs substrate. Therefore, the ALE growth mechanism of ZnTe and ZnSe



Fig. 3.

RHEED patterns during the deposition of ZnTe by ALE. (k || [110]) (a)GaAs substrate after thermally cleaned and cooled down to 230°C. (b)Zn-covered surface after depositing 10 monolayers. (c)after depositing 50 monolayers. (d)after depositing 200 monolayers.









### Fig. 4.

RHEED patterns during the deposition of ZnTe by MBE. (k || [110]) (a)GaAs substrate after thermally cleaned and cooled down to 250°C. (b)after depositing 10s. (c)after depositing 25min. (d)after depositing 2hr.

heteroepitaxially on (001)GaAs substrate is of Stranski-Krastanov type.

IT is interesting to compare the crystallinity of epilayers grown by moleuclar beam epitaxy (MBE) and ALE. Figures 4(a)-(d) show RHEED patterns of ZnTe grown by MBE on (001)GaAs substrate at 250°C, a little higher substrate temmperature than the ALE described above. The molecular beam intensities of Zn and Te<sub>2</sub> in MBE are fixed at the same values as those in ALE. Although the thermally cleaned substrate surface is very smooth as indicated by the streaky RHEED pattern (Fig.4(a)), the 10sec deposition of ZnTe layer (thickness  $\sim 15 Å$ ) generated a spotty pattern (Fig.4(b)) with slight streaks which are indicative of three-dimensional growth mechanism at such low substrate temperature. After 25min

deposition, the spotty pattern became prominent (Fig.4(c)), and eventually, excess spots due to the growth of twinned crystal were observed (Fig.4(d)). Comparing Figs.3 and 4, we can draw a conclusion that the epitaxial temperature can be lowered by ALE than MBE.

# 4. Fabrication of (ZnSe) (ZnTe) superlattice

We have grown  $(ZnSe)_m(ZnTe)_n$  superlattice on (001)GaAs substrate at 280°C, where m monolayers of ZnSe and n monolayers of ZnTe are deposited alternately. In order to grow m ZnSe layers, the number of opening and closing cycles of Zn and Se sources is m. Therefore, we can fabricate  $(ZnSe)_m(ZnTe)_n$  superlattice by repeating the m cycles of ZnSe layers and n cycles of ZnTe layers.

In order to obtain a smooth interface at the

heterojunction, two-dimensional growth mechanism We grew 1000A thick ZnSe by MBE as is requisite. a buffer layer which showed elongated spotty RHEED pattern (Fig.5(a)). As the deposition of ZnSe and ZnTe procedes by ALE, the streaky pattern becomes prominent. Figures 5(b) and (c) show RHEED pattern (k || [110]) of Zn-covered surface on 50-monolayers-thick ZnTe layer deposited on ZnSe and that of the Te-covered surface. The RHEED patterns exhibit c(1x2) and (2x1) reconstructed surface for Zn- and Se-covered Similar RHEED pattern changes are surfaces. observed from 50 monolayers thick ZnSe layer deposited on the ZnTe layer, that is, c(1x2) for Zn-covered and (2x1) for Se-covered surfaces.

The observed change of the RHEED pattern is indicative of two dimensional growth in ZnTe/ZnSesuperlattice despite the large misfit (7%). Then, it is speculated that the matching in chemical bond nature between the overgrowth and the substrate is crucial for the layer by layer growth in heteroepitaxy of Zn-chalcogenides, rather than the matching in lattice constant. In fact, although there is only a slight lattice misfit (0.25%) between GaAs and ZnSe, the initial stage of the ALE growth of ZnSe is dominated by three dimensional growth mechanism.

We have examined the formation of the superlattice structure for  $(ZnSe)_4(ZnTe)_4$  with X-ray diffraction technique. It was observed that the periodicity of the superlattice is the same as



## 5. Conclusion

We have grown ZnSe and ZnTe films for the first time by ALE, investigated the initial and successive stage of the epitaxy, and tried a fabrication of ZnSe/ZnTe superlattice structure. Followings are found:

- (1)The average thickness per one opening and closing cycle of shutter of a constituent element corresponds to one monolayer thickness.
- (2)The initial stage of heteroepitaxy of Znchalcogenides on GaAs is dominated by threedimensional growth mechanism. When more than 100 monolayers are deposited, two dimensional growth mechanism dominates.
- (3)ALE allows lower substrate temperature than MBE for growth of singlecrystalline films.
- (4)The growth of ZnSe buffer layer on GaAs substrate improves interface quality between ZnSe and ZnTe grown on this buffer layer, which in turn shows excelent feasibility of fabricating superlattice structure by ALE.

### references

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## Fig. 5.

RHEED patterns during the deposition of ZnTe/ZnSe superlattice. (k ||[110]). (a)1000Å thick ZnSe buffer layer grown on GaAs substrate. (b)Zn-covered surface after depositing 50 monolayers of ZnSe on ZnTe. (c)Se-covered surface after depositing 50 monolayers of ZnSe on ZnTe.