Interface studies of molecular beam epitaxy (MBE) grown ZnSe-GaAs heterovalent structures

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Comprehensive investigations on ZnSe/GaAs and GaAs/ZnSe (100) interfaces were carried out by photoluminescence (PL) and transmission electron microscopy (TEM), as an essential building block towards the realization of high quality ZnSe-GaAs heterovalent structures (HS). The nature of ZnSe/GaAs (100) interface with different surface terminations of GaAs was examined. The ZnSe/Ga-terminated GaAs hetero-structure was found to have a superior optical and microstructural quality, with a chemical interface consisting of a mixture of both the GaAs and ZnSe atomic species. For GaAs/ZnSe (100) interface studies, a low-temperature migration enhanced epitaxy (LT-MEE) growth technique was used to grow GaAs layers under the conditions compatible to the growth of ZnSe. Both Ga and As-initialized LT-MEE GaAs/ZnSe interfaces were investigated. A defective transition layer was observed along the As-initialized GaAs/ZnSe interface, which may be attributed to the formation Zn$_3$As$_2$ and related compound. The correlation between the observed optical/structural properties of both the (GaAs/ZnSe and ZnSe/GaAs) interfaces, and the growth conditions used in this study were discussed in detail. This study could provide valuable insight for the research on ZnSe-GaAs HS.
I. INTRODUCTION

Zinc selenide (ZnSe) - Gallium arsenide (GaAs) heterovalent structure (HS) has long been recognized as a potential candidate for fabricating various optoelectronic applications including displays, light emitting diodes, and lasers with optimal chromaticity. Though, the ZnSe-GaAs HS exhibits a low lattice mismatch (0.25% at room temperature) and direct energy gap, the chemical valence mismatch at the ZnSe-GaAs HS interface is a bottleneck to practically integrate these two materials with tolerable interface defect density. The chemical valence mismatch may result in the formation of defect states in the energy band gap of ZnSe-GaAs HS system, which could degrade the radiative emission efficiency of devices. Moreover, these interface imperfections are found to be responsible for the high stacking fault density in ZnSe-GaAs HS, which further degrades the lifetime of devices.

In this regard, extensive investigations were carried out by various authors to understand the nature of ZnSe-GaAs HS interfaces, which include the widely studied ZnSe on GaAs HS (ZnSe/GaAs interface) and the less investigated GaAs on ZnSe HS (GaAs/ZnSe interface). The detailed investigations using capacitance-voltage (CV) and photocurrent spectra (PS) techniques reveal that the ZnSe/Ga-terminated GaAs interface contains the lowest interface defect state density when compared to ZnSe/As-terminated GaAs. Though, the ZnSe/Ga-terminated GaAs interface is electrically good, structurally it found to contain an ultra-thin Ga-Se (Ga$_2$Se$_3$) compound transition layer, which could promote three-dimensional nucleation of subsequently grown ZnSe, resulting in bulk ZnSe with high defect density. In contrast, the electrically poor ZnSe/As-terminated GaAs is reported to contain a transition layer of Zn-As (Zn$_3$As$_2$), which could promote two-dimensional nucleation of ZnSe resulting in bulk ZnSe with low defect density. The formation of these compound Ga$_2$Se$_3$ and Zn$_3$As$_2$ ultra-thin transition layers may be attributed to the reaction between Ga (Zn) and Se (As) atoms during the initial stages of epitaxial deposition of ZnSe on Ga and As-terminated GaAs surfaces.

In contrast to the widely studied ZnSe/GaAs interface, the GaAs/ZnSe interface was rarely investigated due to the fact that the underlying ZnSe decomposes far below the temperatures which are favorable for the conventional MBE growth of GaAs (around 580°C). As a consequence, the GaAs layers had to be grown at low temperatures (around 300°C) which could yield poor crystalline GaAs layers on ZnSe with defective interface. Understanding the structural and optical properties of GaAs/ZnSe interfaces towards the development of ZnSe-GaAs HS is, therefore,
demanding. Moreover, the surface termination of ZnSe and initial layer of GaAs were proven to affect the GaAs/ZnSe interface quality\textsuperscript{4,14-18}, which adds another complexity to examine this interface and hence the development of GaAs/ZnSe HS. It was shown that the initial exposures of ZnSe surface to As or Se atomic fluxes prior to GaAs growth by metalorganic vapor phase epitaxy (MOCVD), will change the interface configuration and affect the band offsets\textsuperscript{4}. In spite of these valuable observations, no detailed interface study of MBE grown GaAs/ZnSe has been carried out. Moreover, no correlation between the interface properties and desired optical performance has been established.

With the aim of developing high quality ZnSe-GaAs HS, a Migration Enhanced Epitaxy (MEE) technique was used to develop GaAs epitaxial layers at temperatures as low as 200°C with good crystalline quality\textsuperscript{20,21}. Previous studies were employed LT-MEE technique to develop ZnSe-GaAs quantum hetero-structures with flat interfaces\textsuperscript{2,3,22-25}. However, these developed ZnSe/GaAs/ZnSe quantum structures were only able to deliver desirable photoluminescence (PL) at extremely low temperatures due to poor crystal and interface quality\textsuperscript{3,22-25}. Understanding the interface properties of ZnSe-GaAs HS, especially the GaAs/ZnSe interfaces using LT-MEE as a growth technique is, therefore, demanding.

In this study, we systematically investigate the structural and optical properties of both the ZnSe/GaAs and GaAs/ZnSe interfaces as an essential building block towards the development of ZnSe-GaAs HS. The interfaces of ZnSe layers grown on the MBE and LT-MEE grown GaAs (100) buffer layers were investigated first. Subsequently the effect of the initial layer of GaAs on the quality of GaAs/ZnSe interface was investigated. Room temperature (RT) PL and transmission electron microscopy (TEM) techniques were used to evaluate the bulk and interface quality of these HS. An attempt has been made to establish a systematic correlation between the observed structural and optical properties of these ZnSe-GaAs HS interfaces in terms of the processing conditions used in this study.

II. EXPERIMENT

All samples were grown in a Varian Gen II MBE system on n-type GaAs (100) substrates, which has etch pit density (EPD) < 500 cm\textsuperscript{-2} from the vendor’s datasheet. Figure 1a and 1b shows the typical stack structures of ZnSe/GaAs and GaAs/ZnSe interfaces used in this study.
TABLE I. Stack structures, growth methods, and growth conditions of the samples used in this study.

| Sample ID | Stack Structure                  | Growth Temperatures       | V/III Ratio of GaAs |
|-----------|----------------------------------|---------------------------|---------------------|
| A         | ZnSe/Ga-terminated GaAs          | 300°C/580°C               | ~15                 |
| B         | ZnSe/As-terminated GaAs          | 300°C/580°C               | ~15                 |
| C         | ZnSe/LT-MBE GaAs                 | 300°C/300°C               | ~1                  |
| D         | ZnSe/LT-MEE GaAs                 | 300°C/300°C               |                     |
| E         | Ga-initialized GaAs/ZnSe         | 300°C/300°C               |                     |
| F         | As-initialized GaAs/ZnSe         | 300°C/300°C               |                     |

Prior to growth, the substrates were first baked in the load-lock chamber at a temperature of 300°C for three hours to remove the water vapor. Subsequently, the GaAs substrates were treated thermally at ~610°C and under As overpressure in the same chamber to remove the native substrate oxide layer. The thermal treatment process was continued until a dot diffraction pattern was confirmed by Reflection High Energy Electron Diffraction (RHEED). In order to provide a better quality of growth surface for ZnSe growth, a 500 nm thick Si-doped GaAs buffer layer was grown on oxide removed GaAs substrates at a temperature of 580°C, and at a V/III flux ratio of ~15. Steaky RHEED with (2 × 4) As-rich pattern was observed during the buffer layer growth. For ZnSe/GaAs interface study, a ~700 thick Ga-doped ZnSe was deposited in the same MBE.
growth chamber at 300°C (Figure 1a). The growth of ZnSe was initiated only after the As background pressure measured by residual gas analyzer (RGA) in the growth chamber was stabilized low enough to improve the crystal purity, since As could incorporate in ZnSe crystal as a dopant. An effusive cell with compound ZnSe source material was used to provide the beam flux for ZnSe growth\textsuperscript{26}. Prior to ZnSe growth, the GaAs buffers with Ga or As surface terminations were confirmed by RHEED reconstruction patterns, including the as-grown $(2 \times 4)$ As-rich surface and $(4 \times 2)$ Ga-rich surface. The $(4 \times 2)$ Ga-rich surface was obtained by annealing GaAs buffer at 560°C in the absence of As ambient. For comparison, a ZnSe/LT-MBE GaAs hetero-structure was also grown, where the LT-MBE GaAs was grown at 300°C and at a V/III $\sim$ 1. The lower V/III $\sim$ 1 is used to prevent excess As incorporation in bulk layer of GaAs at LTs, as excess As in GaAs will be metallic and suppress the radiative recombination\textsuperscript{27}.

With the aim of developing high quality GaAs at LTs for the development of HS, we have initially optimized the LT-MEE GaAs growth conditions for ZnSe/GaAs interface study. The LT-MEE GaAs hetero-structure was grown at 300°C with fixed Ga amount (1 monolayer (ML)) and varying As amount per cycle (Figure 1c)\textsuperscript{20,21}. The relationship between the number of surface sites and beam flux pressure was derived from\textsuperscript{20,21}. For GaAs/ZnSe interface study, $\sim$ 100 nm of LT-MEE GaAs with As and Ga as starting layers were used (Figure 1b). The Ga-initialized growth was simply achieved by starting the growth at 300°C with Ga monolayer on ZnSe surface. As shown in Figure 1d, the As-initialized growth was completed by depositing initial As layers followed by Ga layers at temperatures below 80°C to achieve high As sticking coefficient on ZnSe surface\textsuperscript{3}. In the subsequent process the as-grown sample was annealed in-situ at 300°C for a few minutes until a single-crystal RHEED pattern was confirmed. The list of samples that have been used in this study are tabulated in Table 1 along with the growth conditions.

The grown ZnSe-GaAs hetero-structures were characterized ex-situ using PL and TEM. All PL characterizations were measured by 405 nm excitation laser with maximum power of $\sim$ 51 mW at room temperature. For different incident laser power measurements, the laser power was changed by neutral density filters and calibrated by power meter. The microstructural and interface investigations were carried out using JEOL JEM 2100F-AC TEM, operating at 200 keV. The cross-sectional TEM lamella were prepared using FEI Scios dual-beam focused ion beam (FIB).
FIG. 2. (a) RT PL responses of ZnSe layers on different MBE GaAs buffer layers (sample A, B, C) and (b) RT PL peak responses intensity of ZnSe layers on different LT-MEE GaAs buffer layers. The LT-MEE GaAs layer were grown with different Arsenic amounts per cycle.

III. RESULTS

A. ZnSe/GaAs interface:

1. Photoluminescence investigations:

The investigations in this study were started from the relatively well-studied ZnSe/GaAs interface. ZnSe epitaxial layers with same thickness and doping were grown under identical growth conditions on different surface terminated GaAs (100) buffer layers (samples A, and B in Table 1). The corresponding PL intensity of ZnSe on Ga-terminated GaAs buffer (sample A) was better than As-terminated (sample B), as shown in Figure 2a. Besides, the interface of ZnSe/LT-MBE GaAs was also investigated (sample C), in which the LT-MBE GaAs layer was grown at 300°C and at a V/III ratio ∼ 1 to avoid excess As in bulk material. The LT-MBE GaAs surface indeed compromised the PL intensity greatly (see Figure 2), proving other epitaxy technique than regular MBE is necessary for growing GaAs component for HS at LT.

Considering the PL intensity of ZnSe/Ga-terminated GaAs (sample A) in this study as a standard reference, we moved forward to optimize the MEE growth conditions to fulfill the needs to grow GaAs at growth temperatures compatible to ZnSe. Firstly, the GaAs layer was grown with Ga ~ 1 ML/cycle and As$_4$ ~ 0.5 ML/cycle. However, the resulting PL intensity was nearly as low as the LT-MBE GaAs buffer, although the RHEED pattern remained streaky during growth. This
might be explained by the deficient associativity of As$_4$ at low temperature. In order to verify that, various amount of As$_2$ per cycle was used in the subsequent experiments and it improved the PL intensity as expected (Figure 2b). The ZnSe PL intensity reached optimal value when the As$_2$ dimmers supplied per cycle was precisely equal to the number of surface sites of GaAs (100) surface. From the prospective of PL performance, the optimized ZnSe/LT-MEE GaAs interface (sample D) was nearly has the same quality as the widely believed least defective ZnSe/Ga-terminated GaAs interface (sample A). Therefore, the same optimized growth conditions of LT-MEE GaAs were used in the subsequent studies.

2. **Structural and chemical investigations of ZnSe/Ga-terminated GaAs interface:**

The bulk microstructural and interface quality of ZnSe/GaAs samples which yield best PL response (i.e. sample A) was examined by TEM. Figure 3 shows the corresponding cross-sectional TEM micrographs along the [001] direction as indicated by the selected area diffraction (SAED)
patterns. The results show that both the GaAs and ZnSe bulk epitaxial layers of sample A exhibit superior microstructural quality (see Figure 3a). The nature of ZnSe/Ga-terminated GaAs interface has been examined by weak beam dark field microscopy for operating reflections $g = 200$, and $g = 400$ in Figures 3b and 3c. It should be noted that the weak beam dark field images do not show any complementary (bright and dark) contrast along the interface for $g = 200$ and 400 reflections (indicated by red arrows in Figure 3b and 3c), which is an important observation in the context of ZnSe/GaAs interface studies. This result suggests that the ZnSe/GaAs interface of sample A contains no signature of Ga-Se (i.e. Ga$_2$Se$_3$) compound transition layer formation at the interface.

With aim of understanding the interface structure of the best PL response sample A, high-resolution TEM investigations were carried out for the ZnSe/Ga-terminated GaAs interface (sample A), however, along the [011] orientation. It can be seen that the interface is highly coherent without any misfit dislocations. The chemical composition of these layers across the interface was examined by scanning TEM coupled with the energy dispersive spectroscopy (EDS) in Figure 4b. It should be noted that the composition of ZnSe and GaAs atomic constituents varies abruptly at the interface within a thickness range of $\sim 6$ nm. The Fast Fourier Transform (FFT) obtained from this ultra-thin 6 nm interface layer is provided in Figure 4a, along with the FFTs of the corresponding bulk GaAs and ZnSe layers. It can be seen that all the three FFTs are similar, and especially the FFT obtained from the interface region is not different from the FFTs obtained for ZnSe and GaAs epitaxial layers. This result suggests that the 6 nm interface layer is similar in structure to bulk ZnSe, and GaAs layers, however, chemically it is expected to contain the mixture of GaAs and ZnSe atomic constituents. The corresponding extracted lattice parameters are 0.5769 nm, 0.5702 nm, and 0.5741 nm respectively for the bulk ZnSe, interface layer, and bulk GaAs layer. The TEM results in this work, therefore, suggest that the ZnSe/Ga-terminated GaAs interface (sample A) has a transition layer which is entirely different in nature from the commonly observed Ga$_2$Se$_3$ transition layer. The EDS and high-resolution TEM analyses suggest that the interface layer has a structure similar to ZnSe and GaAs, and contains all the four atomic constituents with variable concentration.
FIG. 4. (a) Cross-sectional high-resolution TEM micrograph of ZnSe/Ga-terminated GaAs hetero-structure (sample A) along [011] orientation. The corresponding FFTs have been acquired at different regions of the image, (b) shows the scanning TEM image of the same hetero-structure along the with the EDS line scan profiles across the interface.

B. GaAs/ZnSe Interface:

1. Photoluminescence investigations:

The GaAs/ZnSe interface has been identified as the bottleneck in the development of ZnSe-GaAs HS. A systematic investigation of GaAs/ZnSe interface, therefore, is essential for the development of HS. In this study, we carefully controlled the initial atomic layer of GaAs on Zn-rich ZnSe surface by the methods mentioned in Section 2. It is observed that both the Ga-initialized GaAs/ZnSe and As-initialized GaAs/ZnSe samples had a decent PL intensity (samples E and F in Table I). Nevertheless, it was difficult to note the absolute value of the intensity quantitatively since the top ∼ 100 nm GaAs layers on ZnSe, absorb the incident laser and excited emission signals. Figure 5a shows the normalized PL peak response intensity as a function of incident laser power obtained from both the samples E and F. The plot is a good qualitative indicator of defect density, since the defect states need to be filled by excited carriers before radiative recombination could happen. At lower incident power, most of the laser energy will be consumed to fill the de-
FIG. 5. Figure 5. (a) RT PL peak responses intensity versus incident laser power from ZnSe layers under different initialized MEE GaAs conditions (sample E and F) and (b) RHEED pattern during MEE GaAs growth on ZnSe

fect states, but the number of defect states is fixed in one given sample. Consequently, the plot will show strong nonlinearity if the defect states dominate. From Figure 5a it should be noted that the As-initialized GaAs/ZnSe (sample F) yields a nonlinear PL response. In contrast, the Ga-initialized GaAs/ZnSe (sample E) yields a more linear PL response. Since the absorption coefficients of both ZnSe and GaAs are high for 405 nm laser which has much higher energy than the band gaps, the corresponding defect states should be near the surface, especially the GaAs/ZnSe interface. This result indicates the more defective nature of As-initialized GaAs/ZnSe interface. Besides, the RHEED pattern shows some transitional behavior from spotty to streaky for both the samples during growth (Figure 5b), suggesting that both the interfaces were not ideally abrupt and flat, and a 3D to 2D growth mode transition might be occurred during the interface formation.

2. Structural investigations:

The structural quality of Ga and As-initialized LT-MEE GaAs/ZnSe interfaces (samples E and F in Table I) were investigated by TEM. Figure 6a and 6b shows the corresponding cross-sectional TEM bright field micrographs along the [012] orientation, and for the operating reflection g = 400. The SAED patterns were acquired from the GaAs/ZnSe interface regions. The following
observations were made from these two micrographs: the interfaces between LT-MEE GaAs and ZnSe layers are quite rough, both MEE GaAs layers are highly defective, and a defective transition region is present beneath the As-initialized GaAs layer (sample F) as indicated by the yellow colored dashed lines in Figure 6b. The poor microstructural quality of MEE GaAs layers could be attributed to low growth temperature and unideal starting growth surfaces involved in this work. The interface quality of MEE GaAs/ZnSe layers were investigated by weak beam dark field microscopy in Figures 6c to 6f. It can be seen that the top thin Ga and As-initialized GaAs layers exhibit bright contrast for \( g = 400 \) operating reflection, and dark contrast for \( g = 200 \) reflection (indicated by red arrows in Figures 6c to 6f).

It should be further noted that the As-initialized GaAs/ZnSe interface exhibits a continuous bright contrast for \( g = 200 \) reflection as indicated by blue arrow in Figure 6f, whereas the bright contrast is absent for Ga-initialized GaAs/ZnSe interface for the same \( g = 200 \) reflection (Figure 6e). Importantly, the bright contrast is absent for \( g = 400 \) reflection in both the MEE GaAs/ZnSe interface layers (Figures 6c and 6d). These observations suggest that the Ga and As-initialized GaAs/ZnSe interfaces (samples E and F) are different in nature. It appears that the non-linear PL behavior of the As-initialized GaAs/ZnSe sample seen in Figure 5a, could be attributed to the defective transition region present along the interface.

IV. DISCUSSION:

The proceeding results revealed that the optical as well as the structural nature of the conventional MBE grown ZnSe/GaAs and LT-MEE GaAs/ZnSe interfaces under a variety of growth conditions. In this section, an attempt has been made to obtain a correlation between the observed properties of interfaces and the growth conditions used in this study.

A. ZnSe/Ga-terminated GaAs interface:

Earlier CV and PS investigations revealed that ZnSe/Ga-terminated GaAs interface has the lowest interface state density\(^{[11][13][14]}\), which was lower than the usual As-terminated GaAs surface obtained under As-rich MBE growth conditions. The results in the current study show that
FIG. 6. Cross-sectional TEM micrographs of the Ga-initialized GaAs/ZnSe and As-initialized GaAs/ZnSe hetero-structures (samples E and F in Table I) along the [012] orientation. (a) & (b) shows the corresponding microstructures acquired under two-beam bright field diffracting conditions and for the $g = 400$ reflection. (c), (d), and (e), (f) shows the images of the same hetero-structures under weak beam dark filed microscopy conditions for $g = 400$ and $200$ operating reflections. The red and blue colored arrows indicate the position of top GaAs layers and the position of GaAs/ZnSe interface.
MBE based ZnSe/Ga-terminated GaAs hetero-structure (sample A) exhibits the best optical performance, with superior microstructural and interface quality when compared to sample B. Many investigators studied the nature of the transition layer which forms at the interface of MBE based ZnSe/Ga-terminated GaAs. It was reported that the transition layer has a structure similar to zinc-blende Ga$_2$Se$_3$ and exhibits a bright and dark contrast at the ZnSe/Ga-terminated GaAs for the operating reflections $g = 200$ and 400 in the weak beam dark field TEM images. In a later study, Dai et al. intentionally deposited a thin Ga$_2$Se$_3$ compound layer on Ga-terminated GaAs surface and observed vacancy ordering in Ga$_2$Se$_3$ layer. The TEM results in the current study reveal no signature of Ga$_2$Se$_3$ at the ZnSe/Ga-terminated GaAs interface. The absence of complementary contrasts along the ZnSe/GaAs interface for $g = 200$ and 400 reflections in dark field TEM images confirm the same (Figure 3b & 3c). Furthermore, the FFT analysis doesn’t reveal any spots corresponding to vacancy ordering at the interface (Figure 4). Importantly, the extracted lattice parameter of the interface (i.e. 0.5702 nm), which is higher than the lattice parameters reported for Ga$_2$Se$_3$ in literature: 0.529 nm, 0.538 nm, suggesting that the interface in this work has a different nature. The extracted lattice parameter of the interface is (0.5702 nm) is comparable to the lattice parameters of bulk ZnSe (0.5769 nm) and GaAs (0.5749 nm) respectively. Chemically, this interface is found to have a thickness of $\sim 6$ nm with the presence of all the four Ga, As, Zn and Se atomic species, suggesting that the interface may be an intermixture of Zn, Ga, As, and Se atoms situated in a zinc-blende structure with variable composition over a range of 6 nm in thickness. No bright contrast is observed for this intermixed layer for $g=002$ and 004 reflections in the TEM dark field images due to close values of atomic scattering factors involved for Zn, Ga, As, and Se atoms.

It appears that the formation of Ga$_2$Se$_3$ layer at the ZnSe/GaAs interface in earlier reports is attributed to the exposure of GaAs surface to Se beam flux prior to the growth of ZnSe. It was also suggested that the formation of Ga$_2$Se$_3$ can be prevented by exposing GaAs surface to Zn beam flux prior to the growth of ZnSe. Moreover, in previous studies the ZnSe/GaAs hetero-structure growth was performed in two separate MBE chambers consisting of III-V and II-VI source materials. After GaAs growth, the as-grown GaAs samples were transferred to II-VI chamber for the subsequent ZnSe growth. Prior to ZnSe growth the GaAs layers are annealed to obtain Ga-rich GaAs surface, typically under the unavoidable ambient of Se. As a consequence, it is reasonable to expect that the reaction between Se and Ga-rich GaAs surface could result in the formation of Ga$_2$Se$_3$ compound layer on GaAs surface. In the present
study, whole growth process was performed in a single MBE III-V growth chamber with compound ZnSe crystal in an effusive cell used as source material. Consequently, when performing annealing process to obtain Ga-rich surface, there are less Se species in the background to react with the GaAs surface, and hence no formation of $Ga_2Se_3$ was observed. Furthermore, it is reasonable to expect that the resulting beam flux from ZnSe compound source is different from the mixture of Zn and Se beams from separate cells. Previous studies also showed the possibility of inter-diffusion of Zn and Ga atoms at the ZnSe/GaAs interface after post-growth annealing. Since the ZnSe growth was done at 300°C for relatively longer time, and the GaAs surface was Ga-rich, the observed 6 nm of intermixed region in this study, thus, could be attributed to the inter-diffusion process of Zn and Ga atomic species across the interface during ZnSe growth.

B. LT-MEE GaAs/ZnSe interface:

In contrast to the ZnSe/GaAs interface discussed above, there were limited available studies on GaAs/ZnSe interface. Since ZnSe decomposes below the typical growth temperatures of GaAs, as a consequence the GaAs epitaxial layer has to be grown at lower temperatures compatible to ZnSe. However, the regular LT-MBE GaAs layers obtained under conditions favorable to ZnSe, exhibit poor crystalline quality and poor optical performance due to incorporation of excess As in GaAs at LTs, and poor mobility of adatoms during growth. Moreover, the chemical valance mismatch at GaAs/ZnSe interface adds further difficulty. Therefore, the GaAs/ZnSe interface has been identified as the bottleneck for the development of ZnSe-GaAs HS. MEE was confirmed to be able to grow GaAs with relatively high quality at low temperature, instead of supplying Ga and As beam simultaneously, it supplies Ga and As beam alternatively to enhance the mobility of Ga adatoms in an As-free environment to maintain stoichiometry and crystal quality. And by employing MEE, one could have more ability to control the interface configuration by different initial modes. As shown in Section. 3, the LT-MEE GaAs/ZnSe interfaces (sample E and F) in this study are relatively rough, and it could be attributed to low mobility of adatoms involved at such low growth temperatures or could be due to a different growth mechanism. The evolution of roughness can be monitored from the transition of RHEED pattern. During the growth of first few monolayers for both the interfaces, the RHEED showed spotty pattern, which can be correlated to the 3D growth mode and the associated interface roughness. Both Ga- and As-initialized GaAs on ZnSe samples (E and F) still showed decent PL, however they exhibited different dependency on
the incident powers of near-surface absorbed excitation laser. The As-initialized GaAs/ZnSe had a more nonlinear dependency, suggesting that it had bigger density of defect states. Moreover, a defective transition region with complementary contrast (bright and dark) was observed along the As-initialized GaAs/ZnSe interface for g = 200 and 400 reflections (sample F). The TEM analysis in this study indicates that the transition region should have a structure factor higher than ZnSe and GaAs for g = 400, and lower than ZnSe and GaAs for g = 200 reflection. As a consequence, in dark field mode this region appears as bright for g = 002 reflection (see Figure 6f) and dark for g = 400 reflections (Figure 6d). Kuo et al.\textsuperscript{28} observed a similar bright contrast region along the ZnSe/GaAs interface for the conditions where the As-stabilized GaAs surface is treated with Zn. It was suggested that the transition region consists of Zn, As and vacancies as constituents and similar to Zn\textsubscript{3}As\textsubscript{2} compound layer\textsuperscript{28}. We believe that the defective transition region observed in this work along As-initialized GaAs/ZnSe interface could be attributed to the formation of Zn\textsubscript{3}As\textsubscript{2} related compound layer.

The main reasons for the formation of Zn\textsubscript{3}As\textsubscript{2} related defective transition region may be the unideal procedure to stick initial As on ZnSe surface at very low temperature\textsuperscript{3}, as well as the following temperature gap between the first few monolayers of As-initialized GaAs growth and the subsequent growth (Figure 1d). The initial As exposure at 80°C to Zn-rich ZnSe surface could result in the formation of a transition region similar to Zn\textsubscript{3}As\textsubscript{2} with the resultant structure factor higher (lower) than ZnSe and GaAs for 200 (400) operating reflections. Secondly, during the temperature ramp-up process prior to annealing and the following growth (Figure 1d), reactions such as interdiffusion\textsuperscript{31} between GaAs and underneath ZnSe could occur, which may further explains the initial spotty RHEED pattern transition and the thickness of the defective region at interface. A similar transition region was not observed along the Ga-initialized GaAs/ZnSe interface (Figure 6e). However, the Ga-initialized GaAs/ZnSe interface (sample E) was not abrupt as well. Earlier studies showed that group III (Ga, In) liquids could form during MBE growth and alter the interface property\textsuperscript{32,33}. Chen et al. showed that during MBE growth of InAs on GaP, initial In-rich nucleation could form liquid layer and dissolve GaP, disabling the growth of an abrupt interface\textsuperscript{32}. Since Ga droplets could form during MBE growth of GaAs on ZnSe\textsuperscript{33} and ZnSe could dissolve in Ga solution\textsuperscript{34}, we believe similar effect could explain the surface roughness: incident Ga atoms during the initial Ga layer formation could “etch” the underneath ZnSe layer and result in rough interface. More investigation will be done following this path.

It is not very clear the detailed influence mechanism of the Zn\textsubscript{3}As\textsubscript{2} transition region on optical
responses described in Figure 5. Nevertheless, the PL response only showed a non-linear behavior for the As-initialized GaAs/ZnSe interface sample, which could be signs of the effect of transition region observed along the As-initialized GaAs/ZnSe interface.

V. CONCLUSIONS:

Systematic investigations on both the ZnSe/GaAs and GaAs/ZnSe interfaces for the realization of ZnSe-GaAs HS were performed using PL and TEM. An optimized MEE procedure using As$_2$, was confirmed to be able to develop the GaAs component of HS with adequate interface quality, resolving the previous challenges on growing LT GaAs while protecting the interface. For ZnSe/GaAs interface, ZnSe/Ga-terminated GaAs has been proven to offer the best interface quality in terms of PL intensity. Detailed TEM investigations excluded the possibility of Ga$_2$Se$_3$ and/or Zn$_3$As$_2$ alloy phase formation at the interface. Instead, an intermixed interface with variable composition was confirmed. For GaAs/ZnSe interface, LT-MEE GaAs with both the As and Ga as initial layers were used. The detailed PL and TEM investigations showed that As-initialized GaAs growth on ZnSe surface yields a more defective interface due to the unideal procedure to stick As on ZnSe surface at low growth temperatures. The TEM investigations suggest that the defective interface of As-initialized GaAs/ZnSe is associated with a transition region similar to Zn$_3$As$_2$. This study could bring more insight to the previous difficulties to obtain good luminescence performance in ZnSe-GaAs quantum structures$^{322}$. The detailed interface study is the essential part to realize high quality HS experimentally. We believe that this work may provide meaningful clues for future studies in this field. Especially, the mechanism behind Ga-initialized GaAs growth on ZnSe could unveil a lot of new possibilities to manipulate the interface geometry.

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