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Sulfur-Passivation Pretreatment of GaAs Surface for Layer-by-Layer Growth and Atomic Layer Epitaxy of ZnSe by MOMBE

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We investigated the growth of ZnSe and ZnSSe in MOMBE on sulfur-passivated GaAs substrates by *in-situ* RHEED monitoring. Layer-by-layer growth was confirmed by streaky patterns and intensity oscillations in RHEED from the very initial stage of the growth, which suggests the possibility of precise control of the thickness of these II-VI epilayers. The growth rate of ZnSe epilayers was higher by 20% on sulfur-passivated substrates than on thermally etched substrates. The sulfur-passivation pretreatment also enabled layer-by-layer growth in the alternate supply of Zn and Se, resulting in ALE growth under H_2 gas supply.

1. Introduction

High-quality substrate surface is strongly required for ZnSe epilayers of device quality. Conventionally, GaAs substrates are deoxidized beforehand at high temperature (>600°C), where surface As atoms evaporate and the resultant GaAs surface is rough and contains many defects. Therefore, novel technique of substrate pretreatment has long been needed.

Recently, chemical treatments with sodium sulfide (Na_2S)[1] or ammonium sulfide (($(NH_4)_2S_x$[2], $(NH_4)_2S$) receive much attention,because of their unique features to improve GaAs surface quality by sulfur-passivation. Especially, the $(NH_4)_2S_x$-treatment enables us to form a smooth GaAs surface by preheating at lower temperatures (260-420°C)[2]. We have reported the properties of high quality ZnSe epilayers on $(NH_4)_2S_x$-treated GaAs substrates[3,4].

In this paper, we describe the effectiveness of $(NH_4)_2S_x$-treated GaAs substrates for layer-by-layer growth of ZnSe and ZnSSe by metalorganic molecular beam epitaxy (MOMBE), including alternate supply of Zn and Se for ZnSe ALE growth.

2. Experimental

ZnSe and ZnSSe epilayers were grown by MOMBE on semi-insulating GaAs substrates. The source materials were dimethylzinc(DMZn), dimethylselenide(DMSe) and hydrogen sulfide (H_2S). They were cracked at 950°C, 850°C and 1080°C, respectively. Reflection high energy electron diffraction (RHEED) was used for *in-situ* monitoring of substrate and epilayer surfaces.

In order to investigate the effect of the sulfur-passivation of GaAs substrates, two methods of treatment, thermal etching and sulfur-passivation, were employed.

[Thermal etching]

After degreasing and etching in H_2SO_4:H_2O_2:H_2O 5:1:1 solution for one minute, the substrate is kept in water to form a clean oxide layer. Then it is loaded into the vacuum chamber, deoxidized at 600-750°C without As overpressure, and cooled down to the growth temperature.

[Sulfur-passivation using $(NH_4)_2S_x$ solution]

After degreasing and the same etching process mentioned above, the substrate is immediately dipped into $(NH_4)_2S_x$ solution for one to several minutes. Then it is loaded into the vacuum chamber, preheated up to 290-420°C to desorb excess sulfur and cooled down to the growth temperature.

The source materials were supplied simultaneously or alternately. In the latter case, we supplied each source for 5 seconds per cycle without interval time, by which we aimed at ZnSe ALE growth.

3. Results and Discussion

3-1 Simultaneous supply growth

After the preheating process, the sulfur-passivated substrate showed streaky RHEED patterns (Fig.1(a)). In the initial stage of the ZnSe growth, we still observed streaky patterns (Figs.1(b) and 1(c)). In the case of thermally etched substrates, the RHEED patterns were spotty before the growth[3], and streaky patterns were hardly observed until the growth of sufficiently thick (≃600A) ZnSe epilayers. These results suggest that the sulfur-passivated GaAs substrates make it possible to grow two-dimensionally from the very beginning of the growth.

Two-dimensional growth of ZnSe on sulfur-passivated GaAs substrate was more strictly confirmed by RHEED intensity oscillation, as shown in Fig.2. A very clear and long oscillation, which suggests highly two-dimensional growth, was observed for the regrowth on 500A ZnSe buffer. (The minimum thickness of ZnSe buffer, on which intensity oscillation was observed, was 120A.) The RHEED intensity oscillation was also observed for $ZnS_{0.30}Se_{0.70}$ epilayer from the initial stage of the growth on 600A ZnSe buffer layer (Fig.3). Therefore, the $(NH_4)_2S_x$-treatment is very effective for precise growth control using *in-situ* RHEED monitoring.

When using the sulfur-passivated GaAs substrate, the growth rate of ZnSe tends to increase. ZnSe epilayers were grown on sulfur-passivated substrates and thermally etched substrates for the same growth time and epilayer thicknesses were compared.

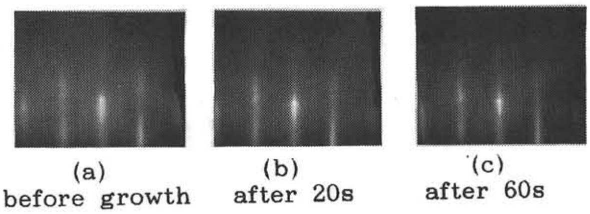

Fig.1 RHEED patterns, along the [110] azimuth, of the initial stage of ZnSe growth onto the sulfur-passivated GaAs substrate. (a):before the growth, (b):20s after initiation of the growth (c):60s after initiation of the growth.

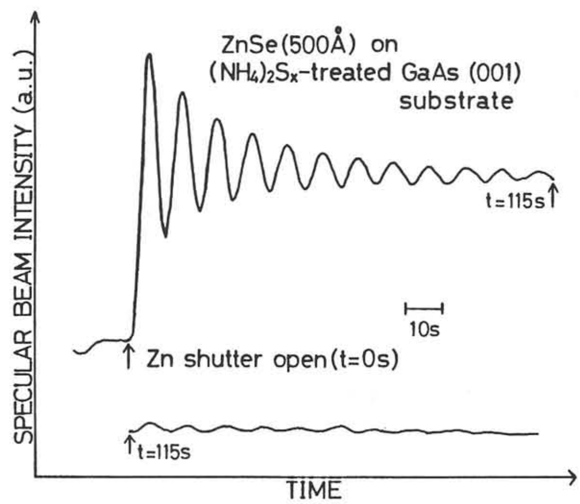

Fig.2 RHEED intensity oscillation for the regrowth of ZnSe on 500A ZnSe buffer layer on the sulfur-passivated GaAs substrate.

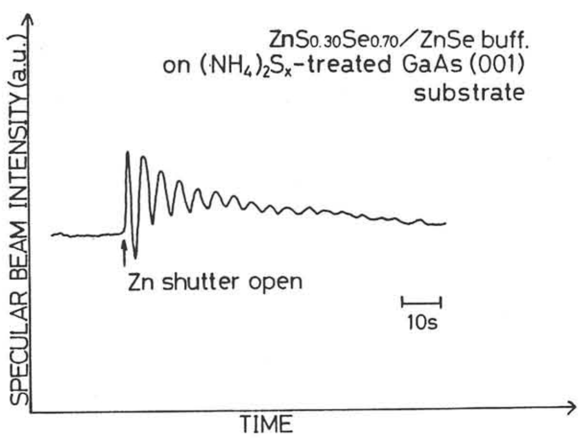

Fig.3 RHEED intensity oscillation for the regrowth of $ZnS_{0.30}Se_{0.70}$ on 600A ZnSe buffer layer on the sulfur-passivated GaAs substrate.

Figure 4 shows that the epilayer thickness increment due to $(NH_4)_2S_x$-treatment was observed not only for thin samples(≃0.03μm) but also for thick samples(≃0.8μm). Figure 5 shows RHEED intensity oscillations for the regrowth onto 1200A-thick ZnSe epilayers. Shorter period of the oscillation for the regrowth onto the sulfur-passivated substrate clearly suggests the higher (≃20%) growth rate compared with the growth on the thermally-etched substrate.

These results suggest that the growth rate is increased not only in the initial stage but also throughout the entire stage of the growth. Further investigation for the surface reconstruction of the substrate and the epilayer is necessary to elucidate the mechanism of the growth rate increase.

3-2 Alternate supply growth

In the first trial, ZnSe epilayers were grown on thermally etched substrates. The growth rate per cycle of source supply is shown in Fig.6 as a function of the growth temperature (T_g). The growth rate was 0.69ML/cycle (T_g=200-230°C). In the initial stage of the growth, the RHEED patterns were spotty, indicating three-dimensional growth. (Fig.7(a))

If we used sulfur-passivated substrates as the next stage, the RHEED patterns were streaky from the initial stage of the growth as shown in Fig.7(b). According to the supply of Zn and Se, the reconstruction patterns exhibited C(2×2) and (2×1), respectively. These results suggest the formation of Zn- and Se-stabilized surfaces during the growth procedure and layer-by-layer growth from the initial stage. However, the growth rate was 0.82ML/cycle, still resulting in incomplete ALE growth. (Fig.6)

We considered that residual methyl-radicals, which combine with Zn or Se atoms due to incomplete cracking, prevented other molecules from sticking nearby and obstructed occurrence of the growth. Therefore we expected that H_2 gas can effectively eliminate these radicals, and increase the growth rate. As a result, $(NH_4)_2S_x$-treatment and H_2 gas introduction realized 0.95ML/cycle growth, resulting in nearly ALE growth. (Fig.6)

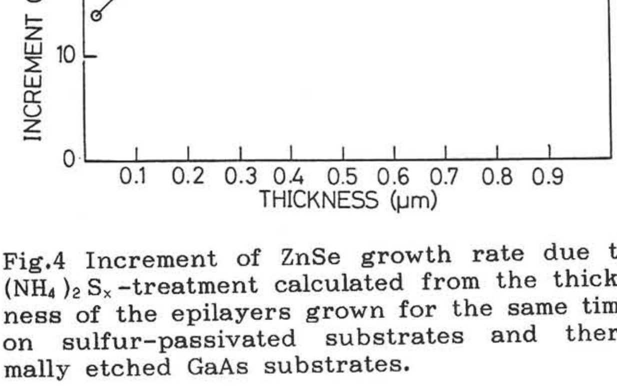

Fig.4 Increment of ZnSe growth rate due to $(NH_4)_2S_x$-treatment calculated from the thickness of the epilayers grown for the same time on sulfur-passivated substrates and thermally etched GaAs substrates.

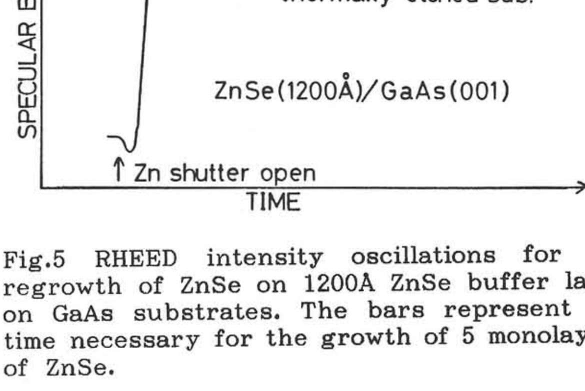

Fig.5 RHEED intensity oscillations for the regrowth of ZnSe on 1200Å ZnSe buffer layer on GaAs substrates. The bars represent the time necessary for the growth of 5 monolayers of ZnSe.

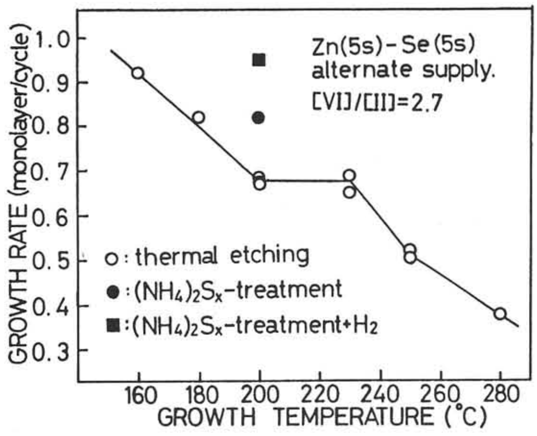

Fig.6 Growth rate of ZnSe, while Zn and Se sources were alternately supplied onto thermally etched substrates (open circle) and the sulfur-passivated substrate (closed circle). The closed square represents the growth rate of ZnSe onto sulfur-passivated substrate under H_2 gas supply.

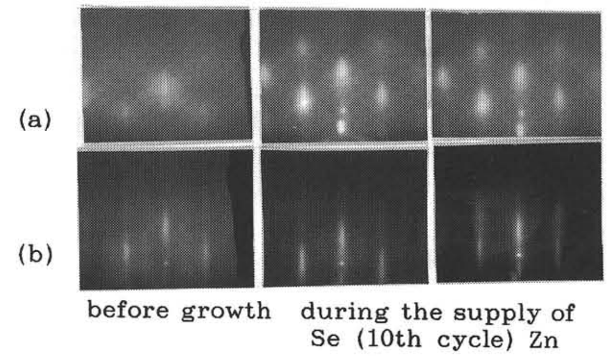

Fig.7 RHEED patterns, along the [110] azimuth, of the initial stage of the growth onto (a) thermally etched GaAs substrate, (b) sulfur-passivated GaAs substrate. (Zn and Se sources are alternately supplied.)

4. Conclusions

Layer-by-layer growth of ZnSe and ZnSSe was realized from the very initial stage by using $(NH_4)_2S_x$-treated GaAs substrates. Therefore, precise control in layer thickness of these II-VI epilayers, which is an essential technique for the fabrication of high-quality short-period II-VI superlattice structures, becomes possible by combination of $(NH_4)_2S_x$-treatment and *in-situ* RHEED monitoring.

However, the $(NH_4)_2S_x$-treatment increased the growth rate of ZnSe by 20%, throughout the entire growth period up to 0.8μm in thickness. This result is considered to be related to some surface structures caused by the $(NH_4)_2S_x$-treatment, but the detail is left to be investigated. In the case of alternate supply of Zn and Se, the $(NH_4)_2S_x$-treatment enabled layer-by-layer growth, resulting in ALE with H_2 gas supply.

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