

Effects of GaAs Surface Pretreatment and Post-Growth Annealing on Interface Properties of MBE-ZnSe/GaAs(Sub.) System

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Interface properties of MBE-ZnSe/GaAs substrate systems formed on variously pretreated GaAs surfaces including standard chemically etched, $(\text{NH}_4)_2\text{S}_x$ -, NH_4I -, HF- and Se-pretreated surfaces, are characterized by C-V and DLTS methods. An HF-pretreated and annealed p-GaAs sample showed marked reduction of interface state density N_{ss} , with $N_{ss,\min} < 4 \times 10^{11} \text{ cm}^{-2}\text{eV}^{-1}$ below the midgap, while C-V curves of n-GaAs samples obtained for the first time indicated the existence of a large N_{ss} above the midgap. DLTS method gave consistent results with C-V method. I- V_{EX} analysis at the interface indicates that V_{EX} exceeds a few volts for a particular U-shaped distribution.

1. INTRODUCTION

Because of availability of its high quality substrate and close lattice constant with ZnSe, GaAs has been widely used as a substrate for MBE growth of ZnSe and related alloys. By using GaAs substrates, successful operation of ZnSe-based blue/green LDs has been demonstrated by many research groups^{1,2)}. However, degradation of the devices and a low electrical-to-optical conversion efficiency due to a high operation voltage are problems for practical use of the devices. It is clear that ZnSe/GaAs substrate interface is one of key points to improve them, because the interface has a strong effect on the quality of epilayer, some degradation phenomena and electrical properties through its composition and structure. So far, influences of initial growth mode³⁾, reconstruction during the growth⁴⁾ and substrate preparation method^{5,6)} on interface state density distribution, N_{ss} , have been studied. However, interface properties are still subject of great interest because they are not well-understood.

The purpose of the present study is to describe the interface properties of MBE-ZnSe/GaAs substrate systems formed on variously pretreated GaAs surfaces, which include standard chemically etched, $(\text{NH}_4)_2\text{S}_x$ -, NH_4I -, HF- and Se-pretreated surfaces, and to describe the effect of post-growth annealing. The influence of interface states on current conduction across the heterointerface is also theoretically analyzed.

2. EXPERIMENTAL

Substrates used in this study were n- and p-GaAs(100) bulk wafers. GaAs was first chemically etched in a $5\text{H}_2\text{SO}_4:1\text{H}_2\text{O}_2:1\text{H}_2\text{O}$ etchant (a subsequent cleaning in a commercial "semicoclean 23" was sometimes employed). Then the substrate was dipped into HF, NH_4I or $(\text{NH}_4)_2\text{S}_x$ solutions for 5-10 min. Thermal cleaning of the pretreated surfaces was carried out at 600°C for 5min without As_4 flux. For Se-pretreatment, a thermally cleaned substrate was irradiated by Se-beam flux at a low temperature ($<130^\circ\text{C}$), and then heated to 500°C . Undoped pseudomorphic ZnSe epilayers were grown at 300°C with Se/Zn flux ratio larger than unity. Post-growth annealing was performed in vacuum, H_2 or N_2 ambients at 400°C for 15 min.

Characterization of grown epilayers and interface properties were made by X-Ray Diffraction(XRD), Raman Scattering, C-V and DLTS measurements. For the electrical characterizations, Au/undoped-ZnSe/n- or p-GaAs "pseudo" MIS systems were used.

3. RESULTS AND DISCUSSION

Figure 1 shows RHEED patterns during the growth sequence of ZnSe on a standard chemically etched substrate and on a Se-pretreated substrate. The nucleation of ZnSe occurred at the beginning of the growth, while gradual elongation to a streaky $c(2 \times 2)$ reconstruction pattern was observed thereafter for the chemically etched sample. Much faster elongation to the streaky pattern was observed for HF-pretreated and $(\text{NH}_4)_2\text{S}_x$ -pretreated samples. A 3-dimensional nucleation in an initial stage of the growth is common feature for Ga-stabilized GaAs substrates. In contrast to those samples, Se-pretreated sample did not indicate the evidence of 3-dimensional nucleation of ZnSe at the beginning of the growth, as seen from Fig. 1.

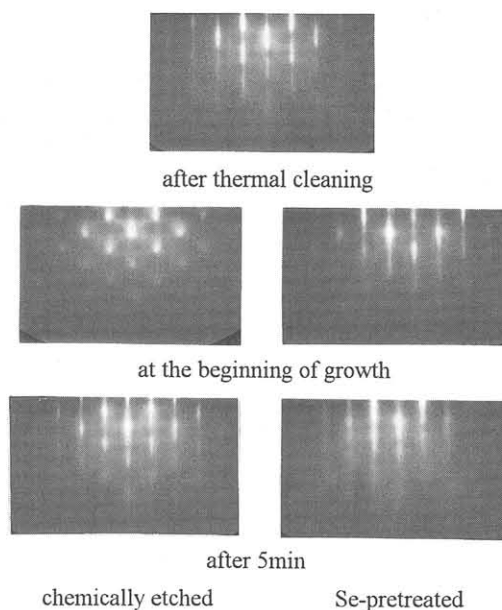


Fig.1 Typical RHEED patterns during the growth sequence.

The lattice constant of the ZnSe epilayer was estimated to be 5.684 Å from the angular splitting between ZnSe(400) and GaAs(400) X-ray diffraction peaks. This value is close to the theoretical one for the pseudomorphic ZnSe epilayer on GaAs substrate, i.e. 5.686 Å, calculated from lattice constants of ZnSe and GaAs, and elastic stiffness constants of ZnSe. Figure 2 compares Raman spectra due to LO phonons, for variously pretreated samples. The data were taken at 300K by using an Ar⁺ laser (4880 Å). Both HF- and (NH₄)₂S_x-pretreated samples gave narrower FWHM with enhanced intensity compared with chemically etched sample, indicating quality of epilayers is improved by these pretreatments. Any change in X-ray diffraction curves and Raman spectra was not observed after the post-growth annealing.

Electrical properties of MBE-ZnSe/GaAs interfaces were assessed by C-V and DLTS measurements. For chemically etched p-GaAs samples, measured C-V curves

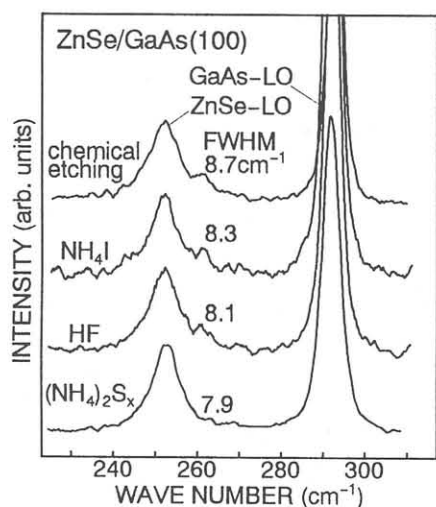


Fig.2 Raman spectra of MBE-ZnSe layers grown on variously pretreated substrates.

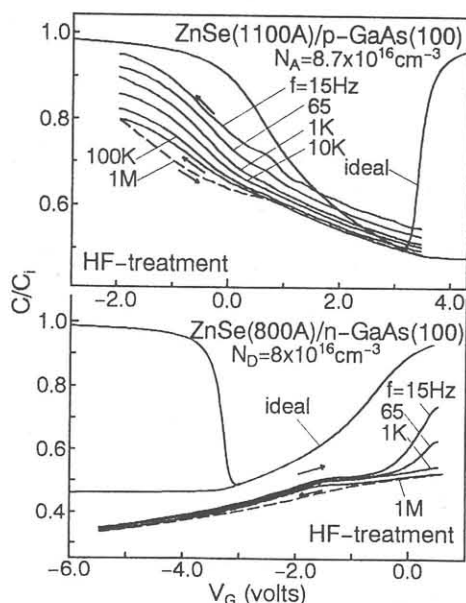


Fig.3 C-V curves of HF-pretreated and annealed MBE-ZnSe/GaAs "pseudo" MIS samples.

are characterized by a large frequency dispersion of capacitance, a counterclockwise hysteresis, and no accumulation nor inversion of carriers. These characteristics are common to GaAs MIS systems, and interpreted in terms of interface states⁷). Effects of the pretreatment of GaAs surfaces and the post-growth annealing were clearly reflected in their C-V curves. Figure 3 shows C-V curves of HF-pretreated and annealed Au/MBE-ZnSe/p- and n-GaAs samples. A 1MHz C-V curve in p-GaAs system become steeper by this pretreatment, with less frequency dispersion of capacitance and less hysteresis width, indicating the improvement of the interface properties. Similar improvement was also obtained in (NH₄)₂S_x-pretreated p-GaAs sample. Calculated N_{ss} using Terman's method are summarized in Fig.4. HF-pretreated and annealed interface showed marked reduction of interface states with N_{ss,min} of 4 × 10¹¹ cm⁻² eV⁻¹ below the midgap. The value is about one order of magnitude smaller than that of the standard chemically etched interface, and comparable to reported N_{ss,min} for (NH₄)₂S_x-pretreated interface⁵). Since appreciable difference of C-V curves between annealing ambients was not observed and since a Se-pretreated p-GaAs sample gave similar N_{ss} value, as shown in Fig.4, formation of a thin intermediary Ga₂Se₃-related layer seems responsible for the improvement of the interface properties by the post-growth annealing.

Since non-equilibrium C-V curves are evident in a large positive bias region for p-GaAs samples, owing to large emission time constants of interface states above the midgap, corresponding apparent N_{ss} distributions are indicated by a bold dashed line in Fig.4. Instead, in order to estimate the interface Fermi level position E_{FS} above the midgap, C-V curves of MBE-ZnSe/n-GaAs samples were examined for the first time. A considerable lowering of accumulation capacitance with frequency was observed in both HF- and (NH₄)₂S_x-pretreated samples, as shown in Fig.3. The result indicates that E_{FS} is not completely unpinned due to a high N_{ss} density above the midgap. E_{FS} was loosely pinned about 0.5-0.6 eV from the conduction band.

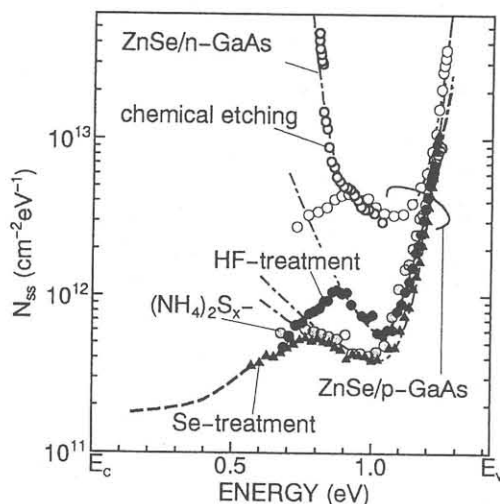


Fig.4 N_{ss} distributions at MBE-ZnSe/GaAs substrate heterointerfaces.

DLTS measurements was performed to confirm the E_{FS} position, since C-V method sometimes misleads the E_{FS} position. Figure 5 shows the resulting Arrhenius plots for the chemically etched samples. Measured bias conditions and the calculated activation energies are indicated in Fig. 5. It is found that DLTS measurements gave consistent results with C-V method in determining E_{FS} .

The influence of interface states on current conduction across the interface is theoretically analyzed. Figure 6(a) shows a model of energy-band diagram with U-

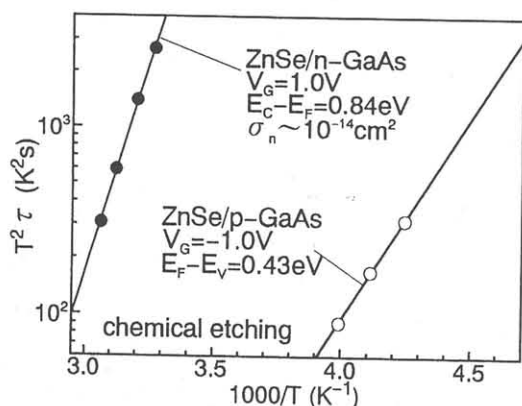
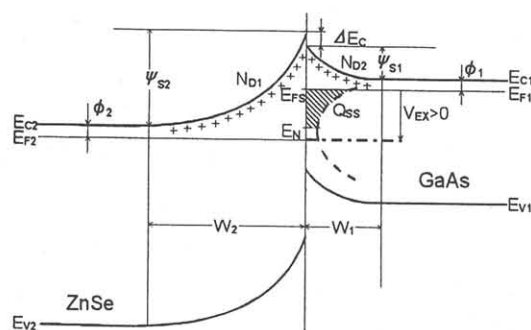
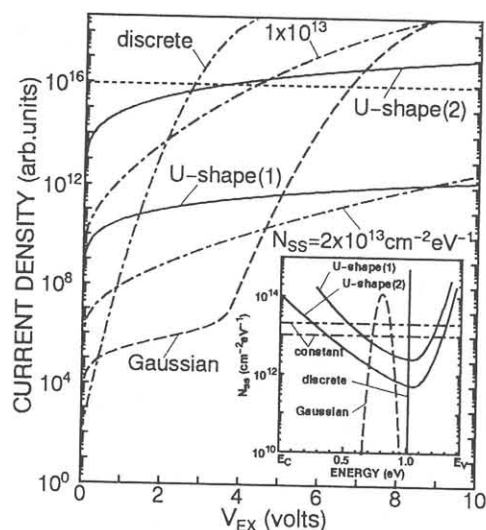


Fig.5 Result of DLTS measurements for chemically etched samples.



(a)



(b)

Fig.6 (a) A model of energy-band diagram and (b) calculated J - V_{EX} characteristics.

shaped N_{ss} distribution, under the condition of excess voltage drop V_{EX} across the interface. Here E_N represents a charge neutrality energy level of the interface states, and located at around the minimum point of the U-shaped distribution. When the occupancy of interface states is dominated by imref of n-GaAs, I - V_{EX} characteristics can be derived from Poisson equation, charge balance equation and energy balance equation based on the thermionic emission theory. Figure 6(b) shows calculated I - V_{EX} characteristics for various N_{ss} distributions shown in the inset. In the calculation, it is assumed that $N_{D1}=N_{D2}=1 \times 10^{18} \text{ cm}^{-3}$ and $E_C - E_N = 1.0 \text{ eV}$. For U-shaped distributions, experimental N_{ss} distributions are extrapolated within the entire bandgap. A current level of 1 kA cm^{-2} , which is estimated from effective Richardson constant for n-GaAs Schottky barrier, is indicated by a horizontal dashed line. It is known that further reduction of N_{ss} density is needed to reduce the operation voltage of LDs or other vertical devices. A comparison with experiment is now undertaken.

4. CONCLUSION

In conclusion, MBE-ZnSe/GaAs substrate systems formed on variously pretreated GaAs surfaces has been characterized. An HF-pretreated p-GaAs sample showed marked reduction of interface state density with $N_{ss, \text{min}} < 4 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$ below the midgap after brief annealing. However, C-V curves of n-GaAs samples obtained for the first time indicated that E_{FS} is not completely unpinned due to a high N_{ss} density above the midgap. DLTS measurements gave consistent results with C-V method in determining E_{FS} . I - V_{EX} analysis at interface indicates that V_{EX} exceeds a few volts for a particular U-shaped distribution.

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