Raman scattering characterization of the crystalline qualities of ZnSe films grown on S-passivated GaAs(100) substrates

J. Wang, X. H. Liu, and Z. S. Li
Surface Physics Laboratory, Fudan University, Shanghai 200433, People's Republic of China

R. Z. Su
Physics Department, Northeast Forestry University, Harbin 150040, People's Republic of China

Z. Ling, W. Z. Cai, X. Y. Hou, and Xun Wang
Surface Physics Laboratory, Fudan University, Shanghai 200433, People's Republic of China,

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A comparative study of the Raman spectra of ZnSe films grown by molecular beam epitaxy on GaAs(100) substrates passivated by $(NH_4)_2S_x$ and S_2Cl_2 solutions is presented. Based on the analysis of the line shape of the first-order longitudinal-optical phonon of ZnSe with spatial correlation model of Raman scattering, it is shown that the ZnSe films grown on the GaAs substrates passivated by S_2Cl_2 solutions have longer coherence lengths, which indicate that their crystalline qualities are better than those passivated by $(NH_4)_2S_x$ solutions. In addition, the barrier heights of ZnSe/GaAs interfaces for different S passivations have been obtained from the ratios of the intensity of the coupled longitudinal-optical phonon-plasmon mode to that of the longitudinal-optical mode of GaAs Raman peak. The results show that the ZnSe/GaAs samples passivated by S_2Cl_2 solutions have lower density of interfacial states. © *1995 American Institute of Physics.*

GaAs has been used as the substrate to grow ZnSe epitaxial layers and other II–VI wide gap materials.[1] In the traditional surface cleaning treatment, the GaAs substrate is heated up to 580 °C in vacuum to thermally remove the native oxide on the GaAs surface. This process results in a Ga-rich GaAs(100) surface. It has been shown that the growth of ZnSe on a Ga-rich GaAs(100) surface might probably form Ga_2Se_3 at the ZnSe/GaAs interface,[2–5] which is the main factor causing the three-dimensional (3D) islanding growth of ZnSe at the initial stage. Guha *et al.*[6,7] have found that the high density of threading dislocations is related to this 3D growth. The above problem might be partially solved by using S passivation to treat the GaAs substrate. A monolayer of sulfur atoms bonded to the substrate atoms is easily obtained by dipping the GaAs wafer in Na_2S-$9H_2O$ or $(NH_4)_2S_x$ solution.[8–11] The effect of S passivation on the ZnSe/GaAs(100) heteroepitaxial growth has been demonstrated by Wu *et al.*[12,13] They found that, by using the treatment of $(NH_4)_2S_x$ solution, the GaAs surface showed a clear streaky reflection high-energy electron diffraction (RHEED) pattern prior to the growth, and the ZnSe film was grown in the layer-by-layer mode from the very beginning as revealed by the RHEED intensity oscillation. The epitaxial ZnSe layer showed specular surface morphology and improved crystallographic and optical properties. Instead of using Na_2S-$9H_2O$ or $(NH_4)_2S_x$ solution, Li *et al.*[14] have developed a new S-passivation method by dipping in an oxygen-free S-containing solution, S_2Cl_2, which can very effectively remove the native oxide of GaAs and is much easier to handle. By using S_2Cl_2 treatment of GaAs substrates, Cai *et al.*[15] have demonstrated the improvement of the crystalline quality of ZnSe films grown by hot wall epitaxy. In this work, the S_2Cl_2 treated GaAs is used as the substrate in the molecular beam epitaxy (MBE) of ZnSe. The crystalline quality of epilayer is measured by Raman scattering. Under the same growth and measuring conditions, we find that the linewidth and line shape of the ZnSe longitudinal-optical (LO) peak are much better, and the forbidden ZnSe transverse-optical (TO) phonon mode is suppressed for the films grown on S_2Cl_2 passivated GaAs substrates in comparison to those grown on $(NH_4)_2S_x$ passivated GaAs surfaces.

Three kinds of GaAs(100) wafers with different doping levels are intentionally chosen as substrates; those are semi-insulating wafers (A), and *n*-type wafers with the doping concentration of 1.0×10^{17} cm^{-3}(B) and n^+-type wafers with the doping concentration of 1.3×10^{18} cm^{-3}(C). The GaAs substrates were first ultrasonically cleaned in trichlorethylene, acetone, and methanol in sequence, followed by a blowing with nitrogen gas for drying. Then, one set of samples (labeled as A_1, B_1, and C_1) were immersed in 60 °C $(NH_4)_2S_x$ solution for 30 min, and rinsed in de-ionized (DI) water. Another set of samples (labeled as A_2, B_2, and C_2) were immersed in $S_2Cl_2+CCl_4$ for 5 s, rinsed in CCl_4 briefly and in flowing DI water. Each pair of GaAs substrates [one passivated by $(NH_4)_2S_x$ and another passivated by S_2Cl_2] was installed on the same sample holder to grow ZnSe films. Prior to ZnSe deposition, the samples were heated to about 380 °C for 10 min, which removed the superflouous sulfur and left the GaAs surface terminated by S–Ga or S–As bonds of submonolayer to one monolayer. The formation of Ga-riched GaAs surface, which usually occurs in ordinary surface treatment method, could thus be avoided. The MBE growth was carried out in a vacuum chamber with the base pressure of 1.2×10^{-7} Pa. The growth condition was optimized with the substrate temperature of 250 °C and growth rate of 0.28 nm/s. The thickness of the epilayer was around 1 μm.

Raman scattering measurements were performed at room temperature on a Jobin Yvon U1000 spectrometer in the

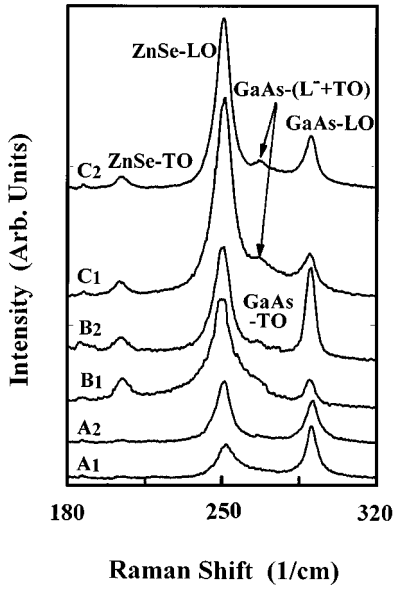

FIG. 1. Raman spectra of ZnSe films grown on GaAs(100) substrates with S passivations. The samples signed A, B, and C are for the GaAs substrates with semi-insulating *n*-type doping concentrations of 1.0×10^{16} and 1.3×10^{18} cm^{-3}, respectively. The samples signed 1 and 2 are passivated by $(NH_4)_2S_x$ and S_2Cl_2 solutions, respectively.

backscattering geometry. The 488 nm line of an Ar^+ laser was used as the excitation source.

Figure 1 shows the Raman spectra of ZnSe films grown on GaAs substrates passivated by $(NH_4)_2S_x$ solution (A_1, B_1, and C_1) and by S_2Cl_2 solutions (A_2, B_2, and C_2). For samples A_1, A_2, B_1, and B_2, the four peaks around 205, 253, 268, and 291 cm^{-1} originate from the ZnSe-TO, ZnSe-LO, GaAs-TO, and GaAs-LO phonon modes, respectively. For samples C_1 and C_2, in addition to the above modes, another peak marked by L^- appears at the position of about 269 cm^{-1}, which is caused by the scattering from the coupled phonon-plasmon modes. The LO/L^- ratios are about 7.7 and 6.8 for samples C_1 and C_2, respectively.

The appearance of the theoretically forbidden TO mode of ZnSe(100) epilayer has been proposed due to the existence of (111) twin crystals in the epilayer.[16] Thus the ZnSe TO/LO intensity ratio is related to the crystalline quality of ZnSe epilayer. Figure 1 shows that the ZnSe TO/LO intensity ratios in the curves A_2 and B_2 are suppressed as compared with those in curves A_1 and B_1, respectively. The ZnSe TO/LO intensity ratios in the curves C_2 and C_1 are about the same. The values of the ZnSe TO/LO intensity ratios are listed in Table I.

The line shape symmetry and the full width at half-maximum (FWHM) of the ZnSe-LO phonon are also associated with the crystalline quality of the ZnSe epilayer. The measured values of FWHMs and the ratios of the left-to-right halves of the peak (Γ_a/Γ_b) are also listed in Table I. In order to quantitatively correlate the crystalline quality with the line shape and FWHM of Raman spectra, the spatial correlation model of Raman scattering has been suggested by introducing a parameter called the coherence length, which is considered as the average size of perfect regions.[16–19]

TABLE I. The values of FWHM, Γ_a/Γ_b, *L*, and ZnSe TO/LO intensity ratios of samples.

Sample	A_1	A_2	B_1	B_2	C_1	C_2
R (TO/LO)	0.062	0.032	0.11	0.064	0.053	0.049
FWHM (cm^{-1})	10.2	7.2	9.8	7.3	5.8	5.2
Γ_a/Γ_b	1.5	1.3	1.5	1.3	1.1	1.0
L (nm)	5.0	7.1	5.1	7.0	9.2	15.5

For our samples, the coherence lengths *L* derived from the experimental values of FWHM and Γ_a/Γ_b are listed in Table I. The values of FWHM, Γ_a/Γ_b and *L* of samples with S_2Cl_2 passivations are better than those of samples with $(NH_4)_2S_x$ passivations. Furthermore, it has been demonstrated that the crystalline quality of ZnSe grown on a $(NH_4)_2S_x$ passivated GaAs substrate is superior than that of ordinarily treated GaAs substrate.[12,13,20] In our work, we also found that the values of FWHM, Γ_a/Γ_b and *L* of samples grown on GaAs treated by $5H_2SO_4$:H_2O_2:H_2O are rather scattered, and are inferior to those obtained on S_2Cl_2 treated substrate.

It is known that a surface barrier exists on the GaAs substrate surface due to the pinning of Fermi level at the surface states. The deposition of ZnSe on GaAs surface may also change that barrier height. One of the effects of S passivation is to reduce the density of surface states and thus to recover the energy band into flatband at the surface region or at least to lower the barrier height.

Raman scattering also provides a quantitative measurement of the barrier height associated with the density of ZnSe/GaAs interface surfaces.[2,21] Since ZnSe material is almost transparent to 488 nm radiation, the Raman signals of GaAs substrates can be observed in Fig. 1. In the highly doped GaAs materials, the LO phonon couples with the free-electron plasma, which induces a LO coupled phonon-plasmon peak L^-. For our samples C_1 and C_2 with n^+-type doping concentration of 1.3×10^{18} cm^{-3}, the width of surface depletion layer δ is smaller than the penetration depth *D* (about 80 nm) of the light of 488 nm,[22] thus only the uncoupled LO phonon will be excited in the surface depletion region and the LO coupled phonon-plasmon peak L^- comes from the GaAs bulk. In this case, the intensity I(LO) of LO phonon is given by[21,23]

$$I(\mathrm{LO}) = I_0(\mathrm{LO})[1-\exp(-2\delta/D)], \tag{1}$$

where I_0(LO) is the LO phonon intensity of the undoped GaAs. Similarly the intensity $I(L^-)$ of the L^- phonon-plasmon peak is given by

$$I(L^-) = I_0(L^-)\exp(-2\delta/D), \tag{2}$$

where $I_0(L^-)$ would be the intensity of L^- peak if there is no depletion layer. Taking the ratio of Eqs. (1) and (2) gives

$$I(\mathrm{LO})/I(L^-) = [I_0(\mathrm{LO})/I_0(L^-)] \times[1-\exp(-2\delta/D)]/\exp(-2\delta/D). \tag{3}$$

δ is related with the barrier height V_B by the following expression:[21,23,24]

$$\delta = (\varepsilon_0 V_B/2\pi e^2 n)^{1/2}, \tag{4}$$

where n is the carrier concentration, $\varepsilon_0=13.1$ is the static dielectric constant of GaAs, and e is the electron charge.

The value of $I_0(\mathrm{LO})/I_0(L^-)=1.49$ for our samples C_1 and C_2 could be interpolated linearly according to Ref. 21. The values of $I(\mathrm{LO})/I(L^-)$ for samples C_1 and C_2 are 7.7 and 6.8, respectively. Based on Eq. (3), the values of depletion width δ for samples C_1 and C_2 are 72.8 and 68.6 nm, respectively. Due the influence of the penetrating depth of light beam, the values of δ obtained here might be overestimated. However, the reduction of depletion width and thus the reduction of barrier height for the sample with S_2Cl_2 passivation as compared with that passivated by $(NH_4)_2S_x$ solution is convincing.

As compared with $(NH_4)_2S_x$, the advantage of using S_2Cl_2 passivation as GaAs substrate treatment technique is quite obvious. The $(NH_4)_2S_x$ treatment requires a relatively long time, i.e., several tens of hours at room temperature or 30–60 min at elevated temperatures of 60 °C. During that period, the oxygen species contained in the $(NH_4)_2S_x$ aqueous solution would react with the GaAs surface, resulting in the replacement of Ga–S bonds by Ga–O bonds and thus causing the partial failure of S passivation. In contrast, $S_2Cl_2+CCl_4$ is an oxygen-free solution and is a very strong etchant for GaAs native oxides. The passivation process could be completed within a very short time interval, thus it can also reduce the foreign atom contamination.

In conclusion, we have used Raman scattering to quantitatively study the crystalline qualities and interface barrier heights of ZnSe/GaAs films with passivations of S_2Cl_2 and $(NH_4)_2S_x$ solutions. The experimental results show that the crystalline qualities of ZnSe epilayers grown on the GaAs(100) substrates with passivation of S_2Cl_2 are better than those passivated by $(NH_4)_2S_x$ solutions. Furthermore, the decreases of densities of interfacial states of ZnSe/GaAs samples with treatment of S_2Cl_2 are found by Raman spectra.

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