

Raman Scattering Characterization of the Crystalline Qualities of ZnSe Films Grown on S-Passivated GaAs(100) Substrates

J.Wang, X.H.Liu, Z.S.Li, Z.Ling, X.Y.Hou and Xun Wang
Surface Physics Laboratory, Fudan University, Shanghai 200433, China
Tel:(0086)-(21)-5490593 Fax:(0086)-(21)-5493232

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 and causes the three-dimensional(3D) islanding growth of ZnSe at the initial stage. The high density of threading dislocations is related to this 3D growth. The above problem might be partially solved by using the S-passivation ($Na_2S{\cdot}9H_20$ or $(NH_4)_2S_x$ solution) to treat the GaAs substrate. The effect of $(NH_4)_2S_x$ passivation for the ZnSe/GaAs(100) heteroepitaxial growth has been demonstrated. In stead of using $Na_2S{\cdot}9H_20$ or $(NH_4)_2S_x$ solution, we have developed a new S-passivation method by dipping in an oxygen-free S-containing solution, S_2Cl_2. In this work, the S_2Cl_2 treated GaAs is used as the substrate in the molecular beam epitaxy of ZnSe, and the crystalline quality of epilayer is studied by Raman scattering.

Three kinds of GaAs(100) wafers are chosen as substrates, those are semi-insulating wafers(A), and n-type wafers with the doping concentration of $1.0{\times}10^{17}cm^{-3}$(B) and $1.3{\times}10^{18}cm^{-3}$(C). The GaAs substrates were first ultrasonically cleaned in trichlorethylene, acetone and methanol in sequence. 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 another set of samples (labeled as A_2, B_2 and C_2) were immersed in S_2Cl_2 + CCl_4 for 5 sec.. Each pair of GaAs substrates (one passivated by $(NH_4)_2S_x$ and another passivated by S_2Cl_2) were 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., in which the superfluous sulfur was removed.

Raman scattering measurements were performed at room temperature in the backscattering geometry with 488 nm line of an Ar^+ laser. Fig.1 shows the Raman spectra of ZnSe/GaAs samples passivated by $(NH_4)_2S_x$ solution and S_2Cl_2 solutions. For samples A_1, A_2, B_1 and B_2, the four peaks around 205, 253, 268 and 291cm^{-1} are originated from ZnSe-TO, ZnSe-LO, GaAs-TO and GaAs-LO phonon modes, respectively. For samples C_1 and C_2 with n^+-type doping concentration of $1.3{\times}10^{18}cm^{-3}$, in addition to the above modes, another peak marked by L^- appears at the position of about 269cm^{-1}, which is caused by the scattering from the coupled phonon-plasmon modes of GaAs.

The appearance of forbidden TO mode of ZnSe(100) epilayer is due to the existence of (111) twin-crystals in the epilayers. Thus, ZnSe TO/LO intensity ratio is related to the crystalline quality of ZnSe epilayer. Fig.1 shows that the ZnSe TO/LO intensity ratios in the curves A_2, B_2 and C_2 are suppressed as compared with those in curves A_1, B_1 and C_1, respectively. In addition, the line shape symmetry (Γ_a/Γ_b) and the full width at half maximum (FWHM) of the ZnSe-LO phonon are also associated with the crystalline quality of the ZnSe epilayer. Fig.1 also shows that the FWHM and Γ_a/Γ_b of the ZnSe-LO peak are much better for the films grown on S_2Cl_2 passivated GaAs substrates than those grown on $(NH_4)_2S_x$ passivated GaAs surfaces. The measured values of FWHMs, Γ_a/Γ_b and ZnSe TO/LO intensity ratios are listed in Table I.

It is known that a surface barrier exists on the GaAs substrate surface. One of the effects of S-passivation is to reduce the density of surface states and thus to recover the energy band into flat band at the surface region. Raman scattering also provides a quantitative measurement of the barrier height of ZnSe/GaAs interface. Based on the intensity ratios of $I(LO)/I(L^-)$ of GaAs, the barrier heights of ZnSe/GaAs interfaces could be obtained and the reduction of barrier height is about 0.57eV for the sample with S_2Cl_2 passivation(C_2) as compared with that passivated by $(NH_4)_2S_x$ solution(C_1).

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 minutes at elevated temperature 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. Contrary, 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 and reduces the foreign atom contamination. Thus, the ZnSe/GaAs samples passivated by S_2Cl_2 solutions demonstrate higher crystalline qualities than those passivated by $(NH_4)_2S_x$ solutions.

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)	0.06	0.03	0.11	0.06	0.05	0.05
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

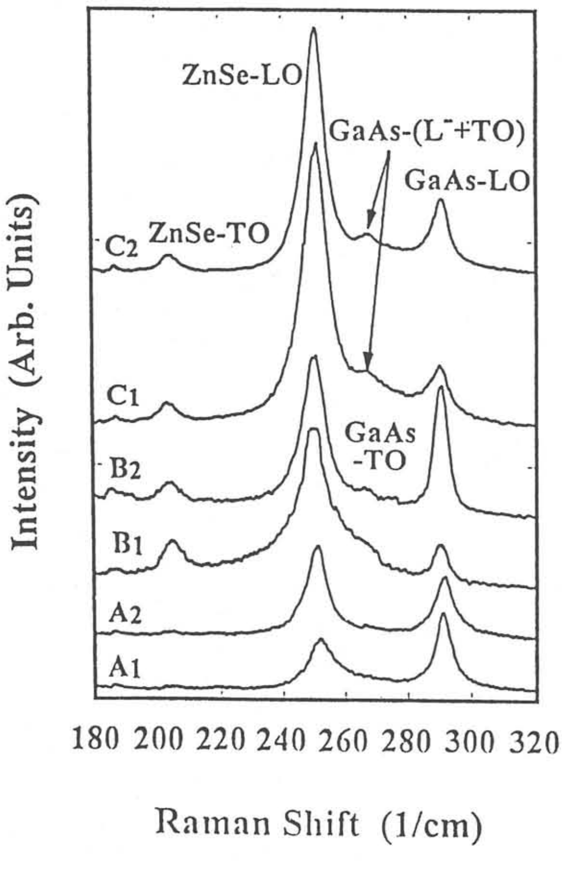

Fig.1. Raman spectra of ZnSe films grown on GaAs(100) substrates with S passivations. The samples signed A, B and C are for the GaAs substrates with semi-insulating, n-type doping concentration of 1.0×10^{16} and 1.3×10^{18} cm^{-3}, respectively. The samples signed 1 and 2 are passivated by $(NH_4)_2S_x$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