Observation of phonon-plasmon coupled modes at the interface between ZnSe and semi-insulating GaAs by micro-Raman spectroscopy

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We demonstrate that the nature of the interface between ZnSe and semi-insulating GaAs can be studied by observing the phonon-plasmon coupled mode by micro-Raman spectroscopy. When the GaAs substrate is sulfur-treated before the growth of ZnSe, the phonon-plasmon coupled mode is clearly observed in micro-Raman spectra. The plasmon is believed to be composed of electrons excited by the focused laser beam used in the micro-Raman measurement. The coupled mode is weak when the substrate is not sulfur-treated. The reduction in the coupled-mode intensity will be due to interface states which widen the depletion layer and shorten the lifetime of excess carriers.

ZnSe/GaAs heterostructures can be utilized for field-effect transistors[1] and nonlinear optical devices.[2] Thus, many researchers have tried to characterize and improve the ZnSe/GaAs interfaces. The interface-state density has been estimated from the capacitance-voltage (*C-V*) characteristics of Au/insulating-ZnSe/*p*-GaAs structures.[3] Olego used the Raman and photoluminescence (PL) spectroscopies to characterize the interface between ZnSe and n^+ GaAs.[4] He estimated the GaAs surface barrier height from the Raman intensities of the unscreened longitudinal-optic (LO) phonon and the LO-plasmon coupled mode.

Very recently, Wu *et al.* reported that the properties of ZnSe/GaAs are greatly improved by the sulfur treatment[5,6] of GaAs before the growth of ZnSe.[7,8] By this treatment, the surface of ZnSe becomes smooth and the luminescence of ZnSe becomes intensive. In addition, the interface state density estimated from the *C-V* characteristics is greatly decreased.[7,9]

In this study, we adopt Raman spectroscopy to study the properties of the interface between ZnSe and semi-insulating (SI) GaAs. Since GaAs is semi-insulating, the unscreened LO phonon is observed by a usual (macroscopic) Raman measurement. On the other hand, when the incident laser beam is focused by a microscope, i.e., the power density is intensified, the optically-excited carrier concentration can be high enough to cause strong phonon-plasmon coupling. The intensity of the coupled mode depends on the depletion layer width in GaAs, and its wavenumber on the concentration of the excited carriers, which is a function of the lifetime of the carriers. Thus, in principle, we can discuss both the Fermi level pinning and the recombination rate of carriers at the interface on the basis of the Raman signal. In this letter, we first show that the LO-plasmon coupled mode is actually observed in the interface between ZnSe and SI GaAs, and then discuss the effects of the sulfur treatment on the interface properties.

ZnSe was grown by metalorganic molecular beam epitaxy at 200 °C on SI GaAs(001) substrates under alternate supply of diethylzinc and dimethylselenium, which were cracked at 950 and 850 °C, respectively. In order to investigate the effects of the sulfur passivation, we used two different methods of GaAs pretreatment. The first one is the conventional treatment. The substrate was etched in $H_2SO_4+H_2O_2+H_2O$ solution and then dipped in water for the formation of an oxide layer. Before the growth, it was deoxidized at 600–750 °C in the growth chamber without As overpressure. The second one includes the $(NH_4)_2S_x$ treatment. After the same etching as above, the substrate was dipped into $(NH_4)_2S_x$ solution and then loaded into the chamber. The excess sulfur was desorbed by a preheating at 290–420 °C before the growth.

The Raman spectra were taken at room temperature in a backscattering configuration. Argon laser radiation at 514.5 nm was used as a light source. ZnSe is transparent for this laser line. In the micro-Raman measurement, the beam is focused through a microscope of 500 magnifications, and the diameter of the laser spot is about 3 μm on the sample surface. The polarization of the incident beam is along $\langle 110 \rangle$ except for Fig. 2(b).

Figure 1(a) shows results of the macroscopic Raman measurement for 1400 Å ZnSe/GaAs. The GaAs substrate was $(NH_4)_2S_x$-treated. The sharp peak at 293 cm^{-1} corresponds to the unscreened LO phonon in GaAs and that at 255 cm^{-1} the LO phonon in ZnSe. The thickness of ZnSe seems below the critical thickness of misfit-dislocation generation, and thus the peak wavenumber is slightly higher than the reported value for bulk ZnSe because of the compressive misfit stress.

Figure 1(b) shows results of the micro-Raman measurement for the same sample. Output power of the laser beam was varied from 35 to 200 mW. The laser power at the sample surface is about 1/10 of the output power. Thus, the output power of 100 mW corresponds to a power density of about 5×10^7 W/cm^2 or a photon flux of about 1.2×10^{23} photons/cm^2 on the sample surface. In comparison with the macroscopic Raman spectrum shown in Fig. 1(a), we note the following differences. (i) The relative intensity of the unscreened GaAs LO phonon is small compared with the ZnSe LO phonon, especially for a large

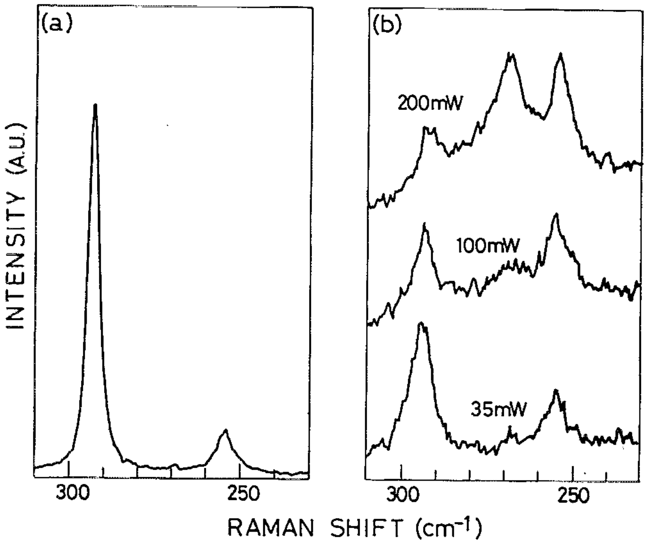

FIG. 1. Raman spectra of 1400 Å ZnSe/GaAs. (a) macro-Raman spectrum. (b) micro-Raman spectra with output power of the light source as a parameter. The output power of 100 mW corresponds to a power density of about 5×10^4 W/cm^2 on the sample surface.

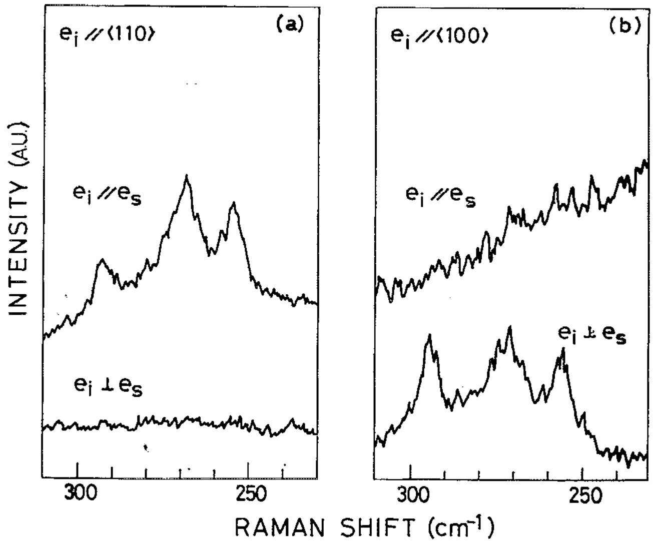

FIG. 2. Analyzed micro-Raman spectra of the same sample as Fig. 1. e_i and e_s represent polarization of the incident and scattered light, respectively.

laser power. (ii) A new peak appears near 270 cm^{-1}, and its intensity increases with the laser power.

These results can be well explained if we consider that the peak near 270 cm^{-1} is due to carriers created by the optical excitation, i.e., the peak corresponds to the LO phonon-plasmon coupled modes in GaAs.[10] The coupled mode has been usually observed in heavily-doped GaAs. It should be noted, on the other hand, that the GaAs substrate of the present sample is semi-insulating; nevertheless the plasmon can be formed of a large density of carriers excited by the focused laser beam. Because of the coupling to the plasmon, the bare LO phonon intensity decreases compared with the macro-measurement.

It is known that the selection rule for the LO phonon also holds for the LO-plasmon coupled modes in a backscattering on a (100) face.[11] Figure 2 shows polarization-analyzed micro-Raman spectra. The laser power is 200 mW, and e_i and e_s represent the polarization of the incident and scattered light, respectively. As shown in the figure, the peak near 270 cm^{-1} actually satisfies the same selection rule as the LO phonon. This also supports our assignment.

The LO-plasmon coupled mode has two branches, and the lower-frequency branch (L^-) approaches the frequency of the TO phonon (270 cm^{-1}) with an increase of the carrier concentration. Thus, the mode observed in Figs. 1 and 2 will be the lower branch. We measured Raman spectra in a wider frequency range in order to observe the higher branch (L^+), but the L^+ mode was not observed. This will be due to a very large width of the L^+ mode signal. The spectrum of the L^+ mode has a much larger width than that of the L^- mode even in the uniformly doped sample. In addition, since the distribution of the photo-excited carriers is not uniform, the L^+ mode peak will broaden further. The broadening due to the carrier distribution will not be significant for the L^- mode, since its peak position hardly depends on the carrier concentration for carrier concentrations larger than 1×10^{18} cm^{-3}.[10]

By an optical excitation, the same number of electrons and holes are excited in the sample. The hole plasmon is damped more strongly than the electron plasmon because of lower mobility of holes, and therefore, we may regard the observed plasma as an electron plasma. Since the L^- frequency is close to the TO frequency, the concentration of the excited electrons is expected to be larger than 1×10^{18} cm^{-3}. We can calculate the lifetime of the excess carries from the excess carrier concentration and the photon flux. Assuming that the diffusion length of carriers is 2 μm, the lifetime of the excess carriers is estimated to be of the order of 1 ns.

For n^+ GaAs, the unscreened LO signal originates in the surface depletion layer. Similarly, the GaAs LO phonon observed in the micro-Raman measurement is due to a thin layer in the interface region which is depleted of carriers because of the Fermi level pinning at the interface. The decrease in the relative intensity of the GaAs LO peak with laser power indicates that the depletion layer thickness decreases with excitation power. Kirillov obtained an empirical relation for evaluating the depletion layer thickness from the intensity ratio of the LO mode to the L^- mode.[12] According to the relation, the depletion layer width is about 10 nm for the output power of 200 mW.

Next, we discuss the effects of the sulfur treatment. Figure 3 shows micro-Raman spectra for two different samples. Sample a was $(NH_4)_2S_x$-treated and sample b was not. ZnSe thicknesses in both the samples are almost the same, about 1200 Å. The LO-plasmon coupled mode is observed for both the samples, but its relative intensity is smaller for sample b. We can consider two reasons for the weakness of the coupled mode. (i) The lifetime of the excess carrier is short, i.e., the interfacial recombination velocity is large, and thus the LO phonon is only partly screened by the excess carriers. (ii) The Fermi level at the

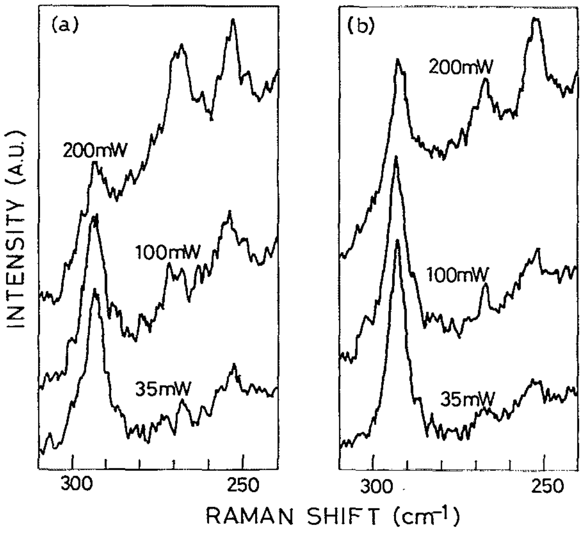

FIG. 3. Micro-Raman spectra of two different 1200 Å ZnSe/GaAs samples. Sample (a) was sulfur-treated and sample (b) was not. The parameter is the output power of the Ar laser.

interface is strongly pinned, and thus the depletion layer does not shrink under the excitation. At present, we cannot determine which factor is dominant. In any case, we may conclude that the weakness of the coupled mode is due to a large interface-state density, since the Fermi level pinning and the interfacial recombination are both caused by gap states at the interface. In fact, it was found by the *C-V* measurement that the interface-state density is much smaller in the $(NH_4)_2S_x$-treated sample than in the sample treated by the conventional method.[7,8] Thus, the nature of the interface can be studied by the present micro-Raman measurement.

For comparison, we carried out the same experiment for a bare SI GaAs substrate, but the LO-plasmon coupled mode was not observed even when the output power was increased to 200 mW. Therefore, the state density of the bare GaAs surface is much larger than that of the ZnSe/GaAs interface treated by $(NH_4)_2S_x$.

The temperature of the samples may rise in the micro-Raman measurement, especially when the laser power is large. The increase in temperature causes broadening of the LO phonon, but this does not influence the main conclusion of this study. We performed the measurement of the low laser power (35 mW) again after the measurement of the high power (200 mW) and found no appreciable change in the spectrum compared to before the high power measurement. Thus, we can exclude from consideration a possibility that the high power measurement causes significant impurity-atom diffusion into GaAs or photothermal decomposition of ZnSe.

In conclusion, we have observed the LO phonon-plasmon coupled mode at the interface between ZnSe and SI GaAs treated with $(NH_4)_2S_x$. The coupled mode is weak in a ZnSe/GaAs structure pretreated by a conventional method and absent in a bare GaAs substrate. The weak intensity of the coupled mode will be due to a large density of the interface states.

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