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Raman Spectroscopic Studies of ZnSe/GaAs Interfaces

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ZnSe/semi-insulating GaAs interfaces have been studied by observing Photogenerated plasmon – LO (PPL) coupled modes by non-resonant micro-Raman spectroscopy. The effect of the carriers generated by the focused laser beam was investigated for a series of different thicknesses of ZnSe epitaxial layers. The PPL mode in GaAs is observed in micro-Raman spectra for all samples, but with different magnitude. The plasma is believed to be electron gas as a result of the negative nature of the interfacial region that contains predominantly hole traps. The free carriers' concentration is estimated to be > 10^{18} cm^{-3} and their life time to be ≈ 0.1 ns. This relatively long lifetime suggests that the ZnSe/GaAs interface has to be of high structural quality leading to low recombination velocity. ZnSe/GaAs heterostructures of less crystalline quality (as determined by resonant Raman measurements) shows the effect of photogenerated carriers only to lesser extent.

1. Introduction:

Modern optoelectronic devices are made up of many layers of different semiconductor materials. The performance depends strongly on both structural quality at the interface and the nature of the space charge zones. In many cases the structural imperfections play a prominent role in the electronic properties of the entire materials. Dislocations, point defects and charge traps are few examples of macroscopic imperfections at the interface.

Raman spectroscopy is the suitable technique for nondestructive characterization of the structural and electronic properties for the substrate side of the interface of large gap / small gap semiconductor heterostructures. A typical example is ZnSe/GaAs heterostructure which has received intense interest through experimental and theoretical studies over the last two decades [1-8] due to its importance in laser action that has been achieved in ZnSe [9] and development electronic devices. In this system, high quality crystals can be grown due to the small lattice mismatch (<0.27%) between ZnSe and GaAs however, a thin ZnSe/GaAs heterostructure suffers internal strains. Typically, the lattice strain relaxes when the overlayer thickness becomes greater than some critical value h_c ($\approx$ 1500 Å) [2]. This relaxation is accompanied by the production of misfit dislocations at the interface along with various point defects such as vacancies and interstitials [10]. Also charge traps associated with defects are believed to exist at ZnSe/GaAs interface [11]. The molecular beam epitaxial growth of thin layers of ZnSe on GaAs results in new charge distribution at the interface, the diffusion of Zn as an acceptor into GaAs and Ga as a donor into ZnSe during sample growth. This produces an intrinsic band bending at the interface [12].

It is known that, in highly doped polar semiconductor the plasma oscillation and the bulk LO phonons couple via their macroscopic electric fields [13]. The coupled modes split into two branches for donor doped semiconductor. The lower branch (L^-) is phonon like with energy close to that of TO phonon and the upper branch (L^+) is plasma like with higher energy. For acceptor doped semiconductor there is only one mode [14]. These modes are Raman allowed and can be observed in the same scattering configurations as for the bulk LO phonons. Unlike the case of carriers created by doping, carriers generated by laser excitation contain both electrons and holes that may couple with LO phonons to form coupled modes. When the incident laser power density is intensified, the optically excited carrier concentration can be high enough to cause strong phonon plasmon coupling in what is called photogenerated plasmon – LO (PPL) coupled modes. This is only possible if the interfacial defect density is sufficiently lowered in order to decrease the recombination velocity for the electron hole pairs at the interface drastically. Furthermore, it is well known that resonance excitation leads to sizable wave-vector (q) dependent contribution to the Raman scattering by LO phonons. These q-dependent scattering are called forbidden scattering and can be used with the overtone scattering to asses the crystalline quality. In this work we used Raman scattering to probe interfacial quality of ZnSe epitaxial layers / semi-insulating (SI) GaAs through the observation of PPL coupled modes and to correlate this quality with the crystal perfection obtained by resonant Raman measurements.

2. Experimental:

The samples used in this study consist of an epitaxial layer of undoped ZnSe (001) grown in a dual chamber molecular beam epitaxy system [15], on a 0.5 μm undoped GaAs (001) epitaxial film terminated with 2×4 surface reconstructures. Five samples of different ZnSe thickness (D_{ZnSe} = 215, 650, 1000, 1330 and 5000 Å) were investigated. All these values are less than h_c (pseudomorphic layers), except the last one which is much larger than the pseudomorphic region (where misfit dislocations are produced at the buried interface as a result of an abrupt strain relaxation). For micro-Raman measurements the spectra were taken at room temperature in back scattering geometry with allowed polarization configuration z(xy)-z where the incident and scattered polarizations are along [100] and [010] crystallographic directions of the samples respectively. The incident radiation is Ar^+ laser at wavelength λ_R = 514.53 nm (2.4 eV) for which ZnSe is transparent while the penetration depth within the GaAs is ≈ 0.1 μm [16]. The beam is focused through a microscope objective on to a 2 μm in diameter circular spot. This yields power densities in the range 5 $kWcm^{-2}$ to 200 $kWcm^{-2}$. For resonant Raman measurements, the spectra were recorded in the forbidden configuration z(xx)-z using Ar^+ laser line 457.9 nm (2.7 eV).

3. Results and Discussion

A typical series of micro-Raman spectra for ZnSe (D_{ZnSe} = 215 Å) on SI GaAs substrate taken at different laser intensities as indicated in Fig. 1. At the lowest intensity 5 $kWcm^{-2}$ two distinct peaks are clearly visible, the sharp peak at 292 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 is 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. Consequently the symmetry selection rules for (001) surfaces are strictly obeyed. The LO scattering intensity for ZnSe increases proportionally to the incident laser intensity as shown in Fig. (1). On the other hand there are dramatic changes in the GaAs features when the intensity is raised. The LO of GaAs decreases in intensity and broadens, while a new peak that appears almost at the same position of the GaAs TO phonon (270 cm^{-1}), builds up as the incident intensity increases. It should be stated that this behaviour was found to be reversible and no damage of the sample was observed even at the highest power density used 200 $kWcm^{-2}$. The dependence of the Raman spectra on the incident light intensity was also observed in the other four samples with different magnitude as will show later.

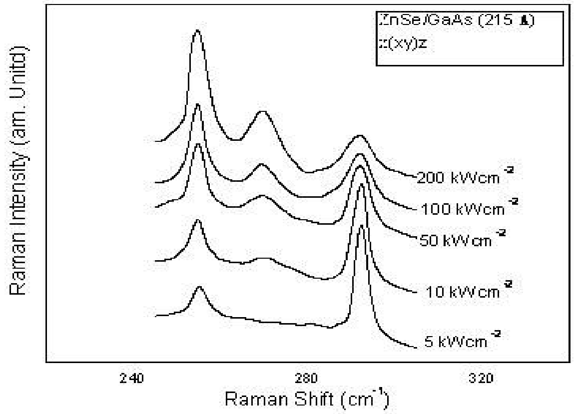

Fig. (1): Micro-Raman spectra of ZnSe/GaAs (D_{ZnSe} = 215 Å) in the z(xy)-z allowed configuration obtained with λ_R = 514.5 nm at different values of incident intensity (as indicated).

The appearance of the scattering near the GaAs forbidden TO phonon which is in combined with the decrease of the GaAs LO phonon can be explained in terms of the creation of the photoexcited carriers in the SI GaAs substrate leads to the observed changes and the formation of photogenerated plasmon – LO (PPL) coupled modes. As was mentioned above the diffusion of Zn as an acceptor into GaAs and Ga as a donor into ZnSe during sample growth produce an intrinsic band bending at the interface. Consequently the photoelectrons created in the GaAs migrate towards the interface while the photogenerated holes get away from the interface. Previous photomodulation Raman scattering measurements of these samples [17] reveal that the interfacial region contains predominantly hole traps. These negatively charged trap states attenuate the interface crossing of the GaAs photoelectrons to ZnSe side. This leads to increasing the electron concentration in the GaAs side near the interface. Noting that the whole plasmon is more strongly damped than the electron plasmon due to their lower mobility therefore, the observed plasma may be regarded as electron plasma.

This plasmon LO coupling results in two new modes (in case of free electrons) denoted by L^- and L^+, where L^- mode approaches the TO phonon frequency (screened LO phonon) as the carrier concentration increase. For wave vectors around 10^6 cm^{-1} and carrier concentration above 10^{18} cm^{-3} the frequency of this mode in GaAs particularly coincide with the TO phonon frequency. Accordingly, the scattering intensity appearing near the frequency of the TO phonon with increasing light intensity in the Raman spectra is assigned to scattering by PPL lower branch (L^-).

Raman spectra in a wider frequency range have been measured in order to observe the higher branch (L^+), but this mode was not observed. This is in line with previous studies [4] which also show that the photoexcited L^+ is difficult to detect in GaAs. This is due to the large width of L^+ in comparison with L^- even in the uniformly doped sample. Furthermore, since the distribution of the photoexcited carriers is not uniform, the L^+ may broaden further. On the other hand the broadening due to the carrier distribution will not be significant for the L^- mode for carrier concentration larger than 10^{18} cm^{-3} [18]. Since the L^- frequency is close to the TO frequency, the concentration of the excited electrons is expected to be larger than 10^{18} cm^{-3}. The lifetime (τ) of the excess carriers can be calculated [19], using $\tau = nd/(I/h\nu)$ where n is the density of the photoelectrons, I is the excitation intensity and d is the skin depth of the incident laser. The lifetime of the excess carriers is estimated to be of the order of 0.1 ns.

The micro-Raman spectra for the other samples show similar behaviour with different magnitude. The variation of the ratio of scattering intensity (I_{L^-}/I_{LO}) versus the incident intensity (I_i) is plotted in Fig. (2) for all samples. This ratio is plotted to focus on the effect of the photogenerated carriers with increasing the intensity of the incident light for different samples. Application of this ratio eliminates other effects such as the interference effect that can be arise from both sides of the ZnSe overlayer [6]. Such effect may lead to oscillatory variations in the scattering intensity with changing the thickness of the overlayer (D_{ZnSe}).

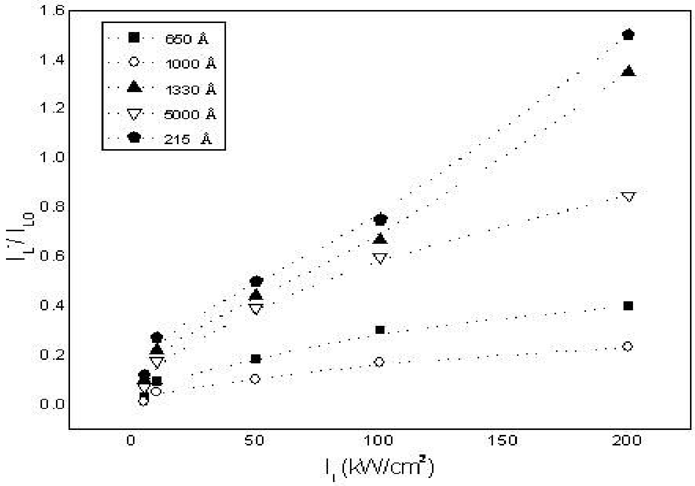

Fig. (2): Scattering intensity ratio (I_{L^-}/I_{LO}) of ZnSe/GaAs obtained with λ_R = 514.5 nm as a function of the incident intensity for different values of D_{ZnSe} (as indicated).

The results show that the PPL coupled modes for the samples of 650 Å and 1000 Å ZnSe overlayer are weak even for the largest intensity used which means that the plasma density is less significant in these two samples as compared to the others. Also the sample of the highest ZnSe overlayer thickness (5000 Å) which is larger than h_c, has a significant larger carriers density, even though there are misfit dislocations appear near the interface for this sample. The spatial inhomogeneity of the free carrier plasma strongly depends on the recombination velocity at the interface, the lower the recombination velocity the better is the homogeneity and the larger the free carrier concentration. Thus it may be concluded from our results that the recombination velocities at samples of D_{ZnSe} (650 Å and 1000 Å) are relatively high. The magnitude of the recombination velocity is determined by the perfection of the interface which itself depend on interfacial abruptness, defect density, interdiffusion, and surface treatment prior to ZnSe growth. All these possibilities may lead to interface states which act as a recombination centers. Thus the occurrence of the PPL modes reflects a high interface quality. Consequently, the data in Fig. 2 can be used to assess interface quality for samples of different D_{ZnSe}.

It is known that the intensity of the forbidden LO-phonon scattering is enhanced by the dominant wave-vector dependent effects due to intera-band scattering that appear at resonance in the diagonal configuration for LO_{ZnSe}. It has been shown [20] that the ratio I_{2LO}/I_{LO} of the 2LO intensity to the LO intensity obtained in the forbidden configuration is sensitive measure of crystal perfection with higher values corresponding to more nearly perfect crystal. For all the samples we observed the ZnSe LO and 2LO phonons in the forbidden configuration z(xx)-z using 457.9 nm (2.7 eV). Figure 3 shows the scattered forbidden LO and allowed 2LO for samples of D_{ZnSe} = (5000 Å & 1000 Å).

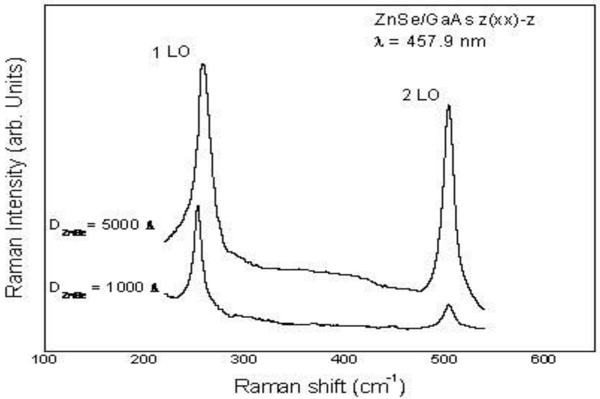

Fig. (3): Raman spectra of ZnSe/GaAs (D_{ZnSe} = 215 Å) in the z(xx)-z forbidden configuration obtained with $\square_{R}$ = 457.9 nm for different values of D_{ZnSe}

Figure (4) shows the ratio I_{2LO}/I_{LO} for the five ZnSe thicknesses. It is clear from the results that the sample with D_{ZnSe} (215 Å, 1330 Å and 5000 Å) are the most perfect crystals among our samples. By comparing the results obtained at resonance with those obtained using non-resonant micro-Raman measurements, we may conclude that, ZnSe/GaAs heterostructures with lower degree of crystal perfection have higher recombination velocities and less significant carrier concentration at the interface. Also samples with high degree of crystal perfection have sufficiently low interfacial defect density that leads to lower the recombination velocity even with the presence of misfit dislocations at the interface as for the case of the sample with D_{ZnSe} = 5000 Å.

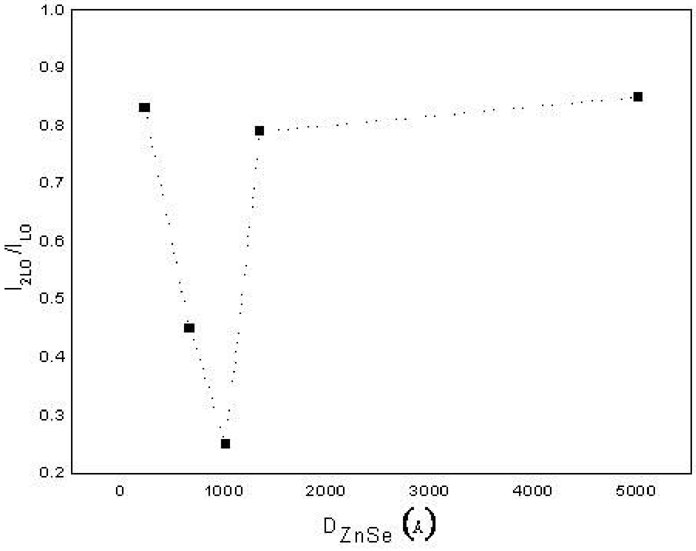

Fig. (4): Scattering intensity ratio (I_{2LO}/I_{LO}) of ZnSe/GaAs obtained with λ_R = 457.9 nm as a function of the ZnSe overlayer thickness D_{ZnSe}

Conclusion:

Strong photoinduced LO phonon plasmon coupled mode was observed at the interface between pseudomorphic ZnSe layer and SI GaAs. The observed plasma was assigned as electron plasma as a result of the presence of negatively charged trap states at this interface. The estimated value of the electron lifetime (≈ 0.1 ns) reveals that the surface recombination rate of the excess carriers is low that reflects the high quality of these interfaces. The ZnSe/GaAs heterostructures of lower degree of crystal perfection showed the effect of photogenerated carriers only to a lesser extent.

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