Interfacial electronic traps at ZnSe/GaAs heterostructures studied by photomodulation Raman scattering

2006 J. Phys.: Condens. Matter 18 4189

(http://iopscience.iop.org/0953-8984/18/17/007)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **18** (2006) 4189–4195 doi:10.1088/0953-8984/18/17/007

Interfacial electronic traps at ZnSe/GaAs heterostructures studied by photomodulation Raman scattering

T A El-Brolossy[1], S Abdalla[2], S Negm[2] and H Talaat[1]

[1] Physics Department, Faculty of Science, Ain Shams University, Cairo, Egypt
[2] Department of Physics and Mathematics, Faculty of Engineering, Banha University, (Shoubra) Cairo, Egypt

Received 26 December 2005
Published 13 April 2006
Online at stacks.iop.org/JPhysCM/18/4189

Abstract

Photomodulation Raman scattering spectroscopy has been employed to study free charge trapping mechanisms at ZnSe–GaAs(001) heterostructure interfaces. This technique reveals that the interfacial region contains predominantly hole traps. Time dependent measurements of the photomodulated Raman scattering intensity show that interfacial charge-trap lifetime is ≈30 s for both electrons and holes.

1. Introduction

Heterostructures of II–VI/III–V semiconductor compounds are particularly attractive because of their potential applications in optoelectronics devices designed for blue emission. Band bending at the interface of such systems is one of the most important factors in device performance since it plays an essential role in determining carrier transport and confinement properties and depends strongly on the interface quality. The structural imperfections such as dislocations, point defects, and charge traps that arise near the junction play a prominent role in affecting the electronic properties of the entire device.

Conventional Raman spectroscopy has been used extensively to characterize non-destructively the structural and electronic properties of deeply buried interfaces, especially in the ZnSe/GaAs heterostructures made up of transparent ZnSe layers (<2.7 eV) on absorbing GaAs (≈1.5 eV) substrates [1–4]. Due to the importance of this system in the laser action [5] and development of other optoelectronic devices, it has received intense interest through experimental [6] and theoretical [7] studies. In the latter, the stability of different interface reconstructions of the (001) interface of this system has been investigated by Kley and Neugebauer for fabrication of high quality interfaces.

The molecular beam epitaxial growth of thin layers of ZnSe on GaAs results in new charge distribution at the interface due to interdiffusion during growth and defects at the interface. The interdiffusion results in interfacial band bending both in GaAs and ZnSe [8]. The associated interfacial electric field induces forbidden LO phonon scattering, namely, the scattering by Franz–Keldysh mechanisms, or simply the 'electric field induced Raman scattering' (EIRS [9]), that can interfere with allowed scattering or be differentiated from it through the known selection rules. In this EIRS the intensity of the signal is proportional to the square of the interfacial field and consequently it can be considered as a direct measure of the potential energy or band bending at the interface.

Although the lattice mismatch in this system is small (0.27% [10]), 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). This relaxation is accompanied by the production of misfit dislocations at the interface along with various point defects such as vacancies and interstitials [11]. Also charge traps are believed to exist at the ZnSe/GaAs interface; however, their nature and origin are not completely understood [12].

Generally, modulation spectroscopy techniques have been powerful methods to study and characterize semiconductor thin films and heterostructures. For example, photoreflectance [13] has been used to investigate the internal electric field of a series of ZnSe/GaAs heterostructures having different layer thicknesses. In particular, photomodulation Raman scattering (PM-RS) spectroscopy [14] has proved to be a very useful technique for providing information about semiconductor surfaces and interfaces that are not available through conventional Raman spectroscopy. In this work we are able to determine the nature of the interface charge traps and to study interfacial trap lifetimes at the ZnSe/GaAs(001) heterojunction. This technique was previously used to study the charge traps at metal–GaAs interface [15] and at n-type GaAs surfaces exposed to air [16]. The PM-RS technique is based on optical perturbation of the interfacial field by illuminating the sample with a second beam of light with energy greater than the bandgap of the material under study, while Raman scattering measurement is in progress. For the heterostructure system of undoped ZnSe/GaAs under study, the diffusion of Zn as an acceptor into GaAs and Ga as a donor into ZnSe during sample growth produces an intrinsic band bending at the interface. Consequently, photons of energy less than the bandgap of ZnSe but larger than the bandgap of GaAs will produce electron–hole pairs in GaAs only, with electrons migrating towards the interface. On the other hand, photons with energies close to the ZnSe bandgap will generate electron–hole pairs in both ZnSe and GaAs with holes (electrons) in ZnSe (GaAs) migrating towards the interface. Some of these carriers will be trapped by charge interfacial defects near the junction and will affect the total interfacial charge. Interfacial trapped holes decrease the interface negative charge and decrease (increase) the band bending at ZnSe (GaAs) side of the junction. Alternatively, interfacial trapped electrons would decrease the positive charge at the interface with a corresponding change in the band bending in each material. These modifications in the band bending are reflected in the measured EIRS intensities in ZnSe and GaAs independently and may allow the determination of the nature of charge traps at the interface.

Also, the combination of photomodulation with Raman scattering allows the determination of interfacial trap lifetime at a ZnSe/GaAs heterojunction. Such a combination provides information about the effects of the interfacial defects on free carriers and provides an example of how modulation techniques can be combined with nonlinear optical spectroscopy to provide low background information about interfaces. Another example of combining photomodulation with nonlinear optical spectroscopies was introduced in the last decade by Yeganeh *et al* through photomodulation of second harmonic generation processes to study interface charge traps (nature, density and lifetime) at ZnSe/GaAs heterostructures [17, 18]. Knowledge about these quantities is essential to fully understand charge transport and carrier lifetime in heterostructures, which in turn may help in better design of photodetectors, diode lasers, and light-emitting diodes.

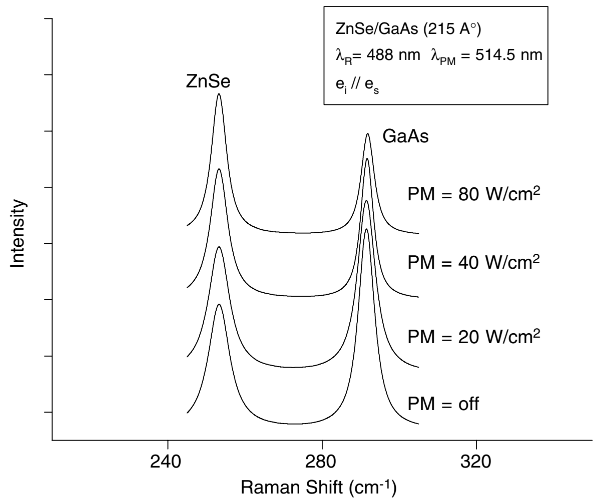

Figure 1. PM-RS spectra of ZnSe/GaAs (215 Å) in the parallel polarization configuration obtained with $\lambda_R = 488$ nm and $\lambda_{PM} = 514.5$ nm at three different values of I_{PM} (as indicated) together with the spectrum without PM.

2. Experimental details

Our samples consist of an epitaxial layer of undoped ZnSe(001) grown in a dual chamber molecular beam epitaxy system [19], on a 0.5 μm undoped GaAs(001) epitaxial film terminated with 2×4 surface reconstructions. The thickness of the ZnSe overlayer (D_{ZnSe}) was 215, 1330 and 5000 Å. These selected values of D_{ZnSe} enabled us to study the interfacial defects in pseudomorphic layers for the first case, where D_{ZnSe} is (215 Å) less than h_c, the second case, where D_{ZnSe} (1330 Å) is of the same order as h_c, and the last case, where D_{ZnSe} (5000 Å) is much larger than the pseudomorphic region where misfit dislocations are produced at the buried interface as a result of an abrupt strain relaxation. The forbidden LO phonon scattered intensities were measured for both GaAs and ZnSe in the parallel polarization configuration of the incident and scattered photons. The incident radiation is an Ar^+ laser at wavelength $\lambda_R = 488$ nm (2.54 eV) with constant intensity I_R (15 W cm^{-2} at the sample surface) while the other wavelengths were used as photomodulating beams (PMBa). Details of the PM-RS experiment are given in [14, 16]. Photoexcited electron–hole pairs were generated in both GaAs and ZnSe when using PM wavelengths $\lambda_{PM} = 457.9$ nm (2.71 eV) while photoexcited carriers were generated in GaAs only for all other wavelengths used. The time dependent PM-RS experiments were designed to measure the trap lifetimes for both electrons (τ_e) and holes (τ_h). The changes in the LO scattering intensities were recorded after the PMB was turned off for both GaAs and ZnSe signals separately. Details of the time dependent measurements are given in [16].

3. Results and discussion

The PM-RS results for the sample of $D_{ZnSe} = 215$ Å, using PMB of $\lambda_{PMB} = 514.5$ nm, with three different intensities I_{PM} (20, 40 and 80 W cm^{-2}) measured at the sample surface, are shown in figure 1, together with the case without a PMB. It is observed that there is a decrease (increase) in the forbidden LO phonon scattering intensity in GaAs (ZnSe) with increasing I_{PM}.

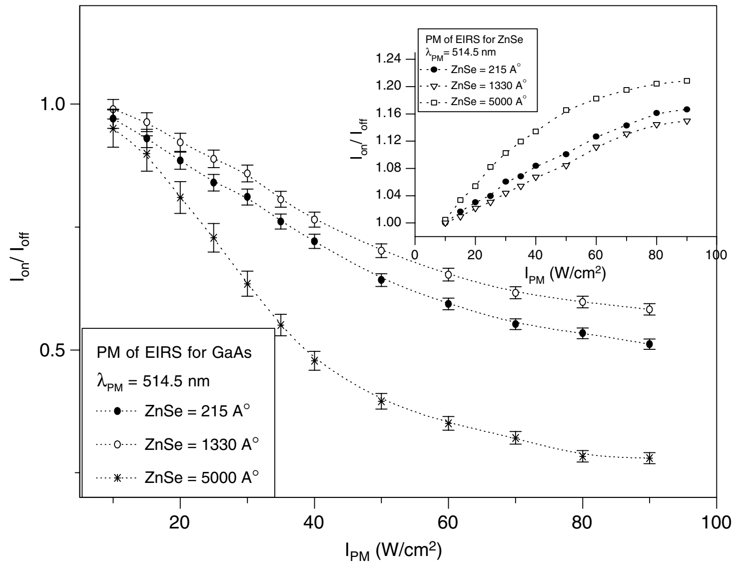

Figure 2. The normalized intensity I_{on}/I_{off} of the forbidden LO_{GaAs} as a function of I_{pm} at $\lambda_{PM} = 514.5$ nm for the three samples of different D_{ZnSe}. The corresponding variation for LO_{ZnSe} is shown in the inset.

The same observations hold for the other samples with $D_{ZnSe} = (1330$ and 5000 Å) under the same conditions. These results could be explained according to the fact that both the PMB as well as the Raman beam generate electron–hole pairs only on the GaAs side of the interface since they have energy larger than the energy gap of GaAs. The generated electrons move towards the interface (trapped) whereas the generated holes move away, decreasing the band bending on the GaAs side. Accordingly, the forbidden LO GaAs scattering intensity decreases. The slight increase in the LO scattering intensity on the ZnSe side is due to the same mechanism that leads us to increase the interface negative charge and consequently the band bending on the ZnSe side of the junction.

The variation of the normalized scattering intensity (I_{on}/I_{off}) versus I_{PM} for GaAs is plotted in figure 2 for the three samples (the results for ZnSe are shown in the inset of figure 2). These results show that the strongest effect of the PM process occurs for the sample of $D_{ZnSe} = 5000$ Å, where the misfit dislocations are present at the interface due to strain relaxation ($D_{ZnSe} > h_c$). Since the PM effect in this case is mostly due to electron traps, these results suggest that the strain relaxation leads to an increase of the electron traps at the ZnSe/GaAs interfaces. Also, it can be seen from the figure that the PM effect is least for the sample of $D_{ZnSe} = 1330$ Å, which may indicate that the number of electron traps at the interface is least as the overlayer thickness becomes close to h_c.

On the other hand, the obtained spectra when using a PMB with energy larger than the bandgap of ZnSe ($\lambda_{PMB} = 457.9$ nm) are shown in figure 3 for the sample of $D_{ZnSe} = 215$ Å at three different intensities of I_{PM} as indicated, together with the case without a PMB for comparison. The results show a decrease (increase) in the forbidden LO phonon scattering intensities of ZnSe (GaAs) with increasing I_{PM}. In this case, PMB is responsible for generation of electron–hole pairs in both ZnSe and GaAs. As was discussed before, the interfacial trapped holes decrease the interface negative charge and decrease (increase) the band bending on the ZnSe (GaAs) side of the junction. Since electrons in GaAs and holes in ZnSe both move

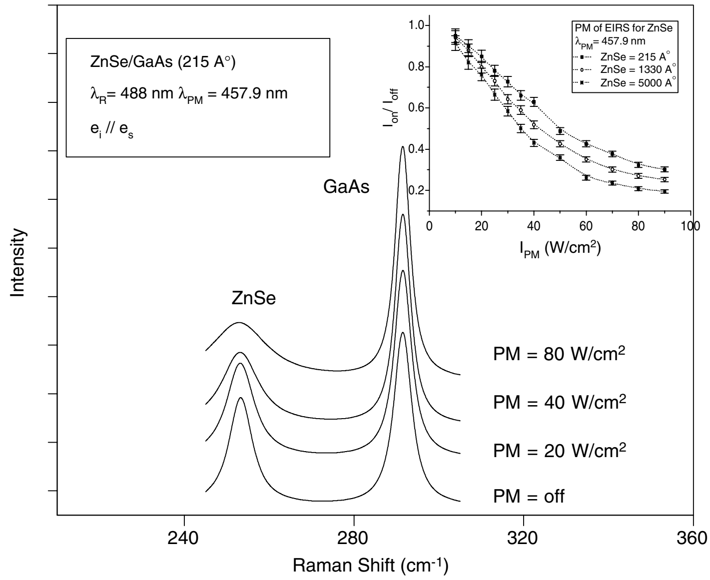

Figure 3. PM-RS spectra of ZnSe/GaAs (215 Å) in the parallel polarization configuration obtained with $\lambda_R = 488$ nm and $\lambda_{PM} = 457.9$ nm at three different values of I_{PM} (as indicated) together with the spectrum without PM. The normalized intensity I_{on}/I_{off} of the forbidden LO_{ZnSe} as a function of I_{PM} for the three samples of different D_{ZnSe} is shown in the inset.

towards the interface, the observations that there is an increase in GaAs signal and a decrease in ZnSe signal suggest that the interface traps are mainly hole traps, i.e. the interface is initially negatively charged. The PM-RS results for the other samples with $\lambda_{PMB} = 457.9$ nm follow the same behaviour as discussed above. Also, the strongest PM effect in this case is for the sample of the largest overlayer thickness (5000 Å), as can be seen from the data presented in the inset of figure 3 for the variation of the normalized intensity of ZnSe versus I_{PM}. This can be explained according to the fact that carriers in this case were generated by PMB almost in ZnSe only (penetration depth of PMB in ZnSe $\approx$ 2600 Å); consequently, the effect of electron traps at the interface is a minimum and the PM effect is mainly controlled by the interfacial hole traps.

The negative nature of the interfacial traps (hole traps) was confirmed by the data in figure 4 that shows the normalized scattering intensity of ZnSe as a function of PMB energy for the three samples at constant $I_{PM} = 20$ W cm^{-2}. Although the efficiency of carrier generation in GaAs is much greater than in ZnSe [20], there is a very small effect as a result of carriers in GaAs only (for energies <2.7 eV) at this intensity level. The slightly larger effect that appears for the sample of $D_{ZnSe} = 5000$ Å in this energy range is due to the increase in the number of electron traps for such a sample, while at energy $>$ 2.7 eV the decrease in the intensity manifests the predominant effect of the hole traps at the interface. This result is in agreement with the prediction of negatively charged bonds at the 2×4 interface [21] and confirmed the observations of Song *et al* [22]. In their work, the modulated photocurrent in ZnSe epilayers grown on GaAs substrate increases only above the ZnSe absorption edge, as a result of the existence of trap states at the interface. On the other hand, our result is not in agreement with the conclusion reported in [23] that the photoexcited plasma in GaAs for ZnSe/semi-insulating GaAs sample was hole gas due to the photoelectrons created in GaAs being easily swept into the ZnSe.

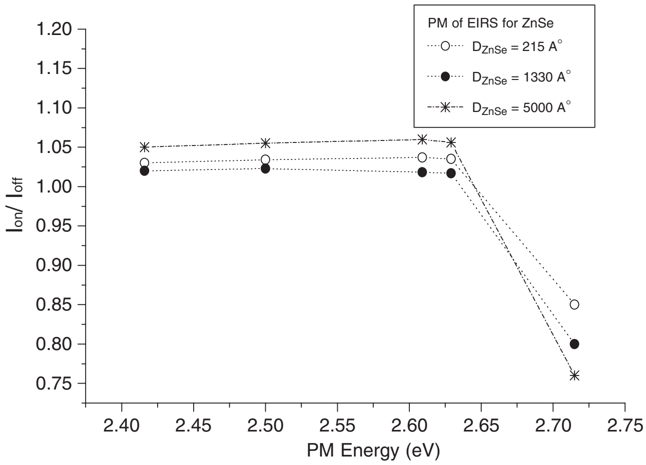

Figure 4. The normalized intensity I_{on}/I_{off} of the forbidden LO_{ZnSe} as a function of PMB energy for the three samples of different D_{ZnSe}. The I_{PM} transmitted into the sample was kept constant at 20 W cm^{-2}.

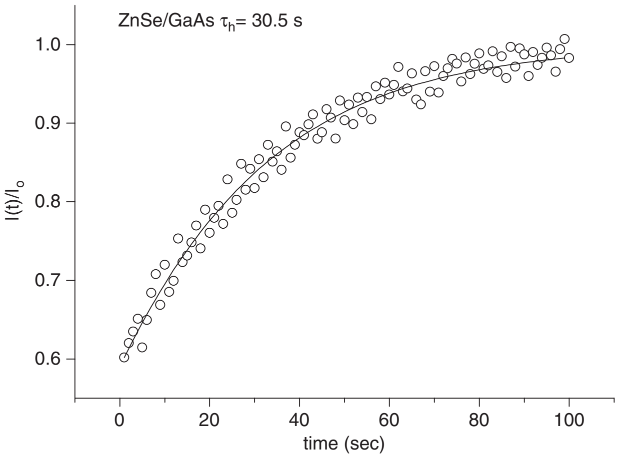

Figure 5. The normalized intensity $I(t)/I_0$ of the forbidden LO_{ZnSe} as a function of time after the PMB (of $\lambda_{PM} = 457.9$ nm) was turned off.

In the time dependent measurements the sample was illuminated for a period of 2 min to ensure that the steady state conditions were reached and then the PMB was turned off ($t = 0$). In this case, the time dependent trapped charge density is given by [16] $P(t) = P_0 \exp(-t/\tau)$, where P_0 is the steady state photogenerated minority carrier density and τ is the trap lifetime at the junction. Consequently, the time dependent intensity ratio $I(t)/I_0$ can be written as $I(t)/I_0 = (1 - A\mathrm{e}^{-t/\tau})^2$, where A is constant.

The photon energy of PMB used in the hole (electron) trap lifetime measurements was 2.71 eV (2.4 eV). The experimental results of the hole trap lifetime (that is τ_h) measurements are displayed in figure 5. The data exhibit a slow recovery time for the Raman scattering intensity. This behaviour was also achieved for the electron trap lifetime. The solid curve in figure 5 is the best fit to the theory. Our fitting routine determined the best value for the recombination of the interfacial trap lifetime. This value was 30.5 ± 0.7 s and 30 ± 0.7 s for hole and electron trap lifetimes respectively. These long lifetimes are characteristic of metastable electronic states typically generated by defects. The surprisingly close values of the electron and hole trap lifetimes are in agreement with other measurements, e.g. that are given by Yeganeh *et al* [18] through the second harmonic generation for the same sample. Furthermore, the trapping and re-emission of the electrons and holes from these slow traps at the ZnSe/n^+ GaAs interface were considered by Ganguli *et al* [24] as the major contribution to the surface photovoltage of the ZnSe thin film above its bandgap.

In conclusion, we have used PM-RS to investigate solid–solid interfaces. Using this technique, we have studied the trapping mechanism at ZnSe–GaAs(001) heterointerfaces. Our results suggest that the interface trap centres are primarily hole traps. We have also used time dependent measurements to determine the lifetime of interfacial traps for both electrons and holes.

Acknowledgment

One of the authors (HT) acknowledges helpful and useful discussions with professor E Burstein (Mary Amanda Wood Professor of Physics Emeritus) at the University of Pennsylvania, Philadelphia, PA, USA.

References

[1] Walsh D, Mazuruk K and Benzaquen M 1987 *Phys. Rev.* B **36** 2883
[2] Olego D 1987 *Appl. Phys. Lett.* **51** 1422
[3] Olego D 1989 *Phys. Rev.* B **39** 12743
[4] Talaat H, Elissa L, Negm S, Burstein E, Yegne M S and Yodh A G 1994 *J. Vac. Sci. Technol.* B **12** 2598
[5] Haase M A, Qiu J, Depuydt J M and Cheng H 1991 *Appl. Phys. Lett.* **59** 1972
[6] Talaat H, Elissa L, Negm S, Burstein E, Yeganeh M S and Yodh A G 1994 *J. Vac. Sci. Technol.* B **12** 2598 and references therein
[7] Kley A and Neugebauer J 1994 *Phys. Rev.* B **50** 8616
[8] Kassel L, Abad H, Garland J W, Raccah P M, Potts J E, Hasse M A and Cheng H 1990 *Appl. Phys. Lett.* **56** 42
[9] Pinczuk A and Burstein E 1968 *Phys. Rev. Lett.* **21** 1073
[10] Yao T 1985 *Technology and Physics of Molecular Beam Epitaxy* ed M G Dowsett and E H C Parker (New York: Plenum) p 313
[11] Labusch R and Schroter W 1980 *Dislocations in Solids* vol 5, ed F R N Nabarro (Amsterdam: North-Holland) p 127
[12] Laks D B, Van de Walle C G, Neumark G F and Pantelides S T 1991 *Phys. Rev. Lett.* **66** 648
[13] Constantino M E and Salazar-Hernandez B 2004 *J. Phys. D: Appl. Phys.* **37** 93
[14] Talaat H, Elissa L, Negm S and Burstein E 1996 *Appl. Surf. Sci.* **104/105** 479
[15] El-Brolossy T A, Abdalla S, Negm S and Talaat H 2005 *Modern Trends in Physics Research* ed L El Nadi (New York: American Institute of Physics)
[16] Talaat H, El-Brolossy T A, Abdalla S and Negm S 2002 *Solid State Commun.* **124** 247
[17] Yeganeh M S, Qi J and Yodh A G 1992 *Phys. Rev. Lett.* **69** 3579
[18] Yeganeh M S, Qi J and Yodh A G 1993 *J. Opt. Soc. Am.* B **10** 2093
[19] Tamargo M C, de Miguel J L, Hwang D M and Farrell H H 1988 *J. Vac. Sci. Technol.* B **6** 784 and references therein
[20] Zhuk B V, Zhukov I A and Zlenko A A 1986 *Solid State Electron.* **29** 247
[21] Farrell H H, Tamargo M C and de Miguel J L 1991 *Appl. Phys. Lett.* **58** 355
[22] Song J H, Sim E D, Joh Y S, Park J H, Baek K S, Oak H N and Chang S K 2002 *Phys. Status Solidi* b **229** 123
[23] Wang F J, Huang D, Wang X J, Gu X X and Yu G C 2002 *J. Phys.: Condens. Matter* **14** 5419
[24] Ganguli T, Kumar S, Kukreja L M and Rustagi K C 2002 *J. Phys.: Condens. Matter* **14** 1813