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Photoluminescence studies on the interaction of near-surface GaAs/$Al_xGa_{1-x}As$ quantum wells with chemical adsorbates

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Abstract

The chemical adsorption of sodium sulphide, ferrocene, hydroquinone and *p*-methyl-nitrobenzene onto the surface of a GaAs/$Al_xGa_{1-x}As$ multiquantum well semiconductor was characterized by steady state and time-resolved photoluminescence (PL) spectroscopy. The changes in the PL response, including the red shift of the emission peak of the exciton in the quantum well and the enhancement of the PL intensity, are discussed in terms of the interactions of the adsorbed molecules with surface states.

Keywords: Chemical adsorption; Multiquantum well; Photoluminescence

1. Introduction

Surface chemistry has both fundamental and technological significance for semiconductor-based devices, such as advanced optoelectronic devices, chemical sensors, solar cells, etc. [1–3]. The chemical adsorption of a variety of organic and inorganic molecules has a considerable influence on the chemical and physical surface properties accompanying the perturbation of the electronic structure; changes in the distribution and occupancy of the surface states and in the electric field of the space charge layer are observed due to the interactions of the semiconductor with the adsorbed molecules. These effects have been the subject of recent investigations [4–10]. The perturbation of the electronic structure of a semiconductor by the adsorption of molecules can be studied by photoluminescence (PL) measurement, which is a sensitive technique for characterizing the optically accessible interface of semiconductors [8,10].

In recent investigations, a quantum well semiconductor has been used as a substitute for a bulk semiconductor to study the surface interaction of molecular adsorption. More information on PL responses induced by chemical adsorption can be obtained in quantum well semiconductor systems due to the size-dependent spectral blue shift arising from energy quantization [11] and the binding energy of the exciton which is altered by both the electric field [12] and the carrier screening effect of the space charge layer [13,14]. In this paper, we report steady state and time-resolved PL studies of the effects of chemical adsorption on the quantum well semiconductor (designed and prepared as a multiquantum well (MQW) structure with near-surface wells of varying thickness).

2. Experimental details

2.1. Materials and chemicals

The lattice-matched GaAs/$Al_xGa_{1-x}As$ MQW samples, consisting of ultrathin alternating layers of GaAs wells and $Al_xGa_{1-x}As$ barriers, were grown on n^+-GaAs(100) (1×10^{18} cm^{-3}) substrates by molecular beam epitaxy (MBE). The structure of the MQW material studied here is as follows: non-intentionally doped epitaxial layers including a 200 nm thick GaAs buffer layer, a 500 nm thick $Al_xGa_{1-x}As$ inner barrier, 11 GaAs quantum well layers with sequential thicknesses of 60, 50, 40, 30, 20, 10, 8, 6, 4, 2 and 1 nm, a 20 nm thick $Al_xGa_{1-x}As$ outer barrier and, finally, a 20 nm thick GaAs capped layer. Each of the quantum wells was separated by a 20 nm thick $Al_xGa_{1-x}As$ barrier layer. The

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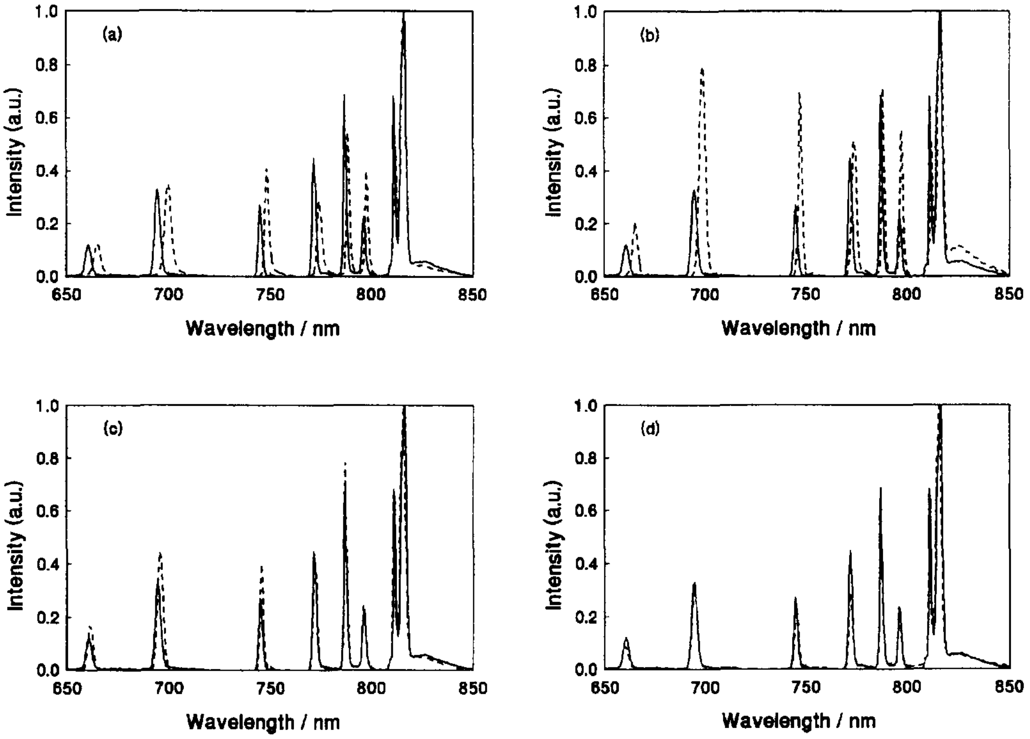

Fig. 1. PL spectra of GaAs/Al$_x$Ga$_{1-x}$As multiquantum well semiconductor modified by inorganic or organic molecules: ———, blank; —, adsorption of following molecules: $Na_2S \cdot 9H_2O$ (a); ferrocene (b); hydroquinone (c); *p*-methyl-nitrobenzene (d).

background carrier concentration of the non-intentionally doped epilayer was about 10^{15} cm^{-3} (n-type). The band gaps of GaAs and Al$_x$Ga$_{1-x}$As determined by PL were 1.519 and 1.960 eV respectively at 10 K. The aluminium fraction x was calculated to be 0.354 according to the empirical formula [15] $E_g^{Al_xGa_{1-x}As} = E_g^{GaAs} + 1.247x$ (eV)

p-Methyl-nitrobenzene (*p*-Me-NB), hydroquinone (HQ), ferrocene (Fc), sodium sulphide ($Na_2S \cdot 9H_2O$), used as adsorbates, were of analytical grade and were used without further purification. Acetonitrile was dehydrated by 4 Å molecular sieves and P_2O_5. Before being covered by adsorbates, the MQW samples were successively ultrasonicated in acetone, alcohol and acetonitrile. Samples (10 μl) of acetonitrile solutions (0.1 M) of *p*-Me-NB, HQ and Fc and aqueous solutions of 0.1 M $Na_2S \cdot 9H_2O$ were dropped onto clean sample surfaces and dried in air. The amount of molecules covering the sample surface was estimated to be 10^{-6} mol cm^{-2}.

2.2. PL measurements

The steady state PL spectra of the MQW specimens were recorded at an excitation wavelength of 632.8 nm using an He–Ne laser with an incident intensity of 2 W cm^{-2}. The time-resolved PL spectra were studied using a Spectra Physics model 171 synchropumping dye laser at a wavelength of 640 nm, which generated 10 ps pulses with a repetition rate of 82 MHz and an average power of 1 mW. A Hamamatsu model 2909 streak camera with a resolution of 32 ps was used for detection. Both steady state and time-resolved PL spectra were measured at 10 K.

3. Results and discussion

3.1. Steady state PL

The PL spectra of MQW specimens with and without adsorption of Na_2S, Fc, HQ and *p*-Me-NB are displayed in Fig. 1. The PL spectrum of the blank sample (full lines in Fig. 1) shows eight sharp emission peaks at positions of 1.519, 1.529, 1.557, 1.576, 1.607, 1.665, 1.785 and 1.877 eV, which are successively produced by bulk GaAs and 20, 10, 8, 6, 4, 2 and 1 nm GaAs quantum wells due to quantum confined effects. The emission peaks of the quantum wells wider than 20 nm overlap with the emission peak of bulk GaAs at 1.519 eV. These emission peaks of the quantum well correspond to the recombination transition of the exciton between an electron and a heavy hole in the lowest eigenstates of each well. The emission peak of the Al$_x$Ga$_{1-x}$As barrier is not observed in these PL spectra. After the adsorption of foreign molecules (Na_2S, Fc, HQ, *p*-Me-NB), as shown in Fig. 1, red shifts in the PL peaks and increases in intensity are observed in the PL spectra for Na_2S-, Fc- and HQ-modified MQW samples; in the PL spectrum of the *p*-Me-NB-modified sample, no distinguishable changes in the PL peaks in terms of position and intensity are observed. The magnitudes of the red shifts follow the order: $Na_2S > Fc > HQ > p$-Me-NB. This trend is illustrated in Fig. 2, which shows the

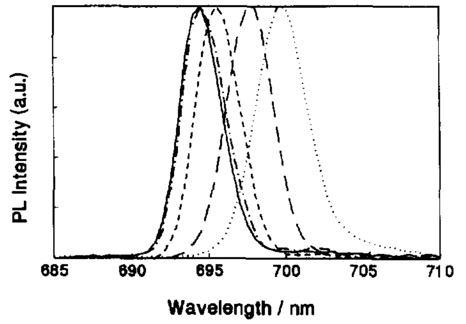

Fig. 2. PL spectra of 2 nm GaAs well in GaAs/Al$_x$Ga$_{1-x}$As MQW structure with and without molecular modification: ———, blank; - - - -, p-methyl-nitrobenzene; – – –, hydroquinone; — — —, ferrocene; · · ·, Na$_2$S·9H$_2$O.

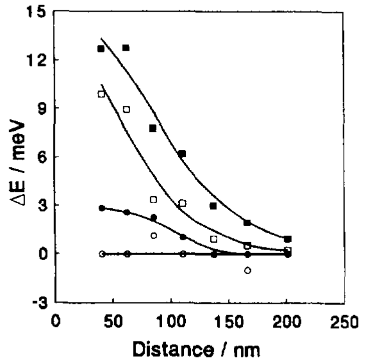

Fig. 3. Relationship between the shifts of the exciton energy level and the distance of the quantum wells to the surface of modified MQW samples: ■, Na$_2$S·9H$_2$O; □, ferrocene; ●, hydroquinone; ○, p-methyl-nitrobenzene.

enlarged emission peak at 1.785 eV produced by the 2 nm GaAs well. The red shifts in the emission peaks of the quantum wells located in the space charge layer region indicate that molecular adsorption changes the properties of the space charge layer. Fig. 3 shows the PL red shifts as a function of distance, illustrating that the PL red shifts occur within a distance of 200 nm from the sample surface and increase with decreasing distance from the wells to the surface. These results indicate that the influence of molecular adsorption on the characteristics of the space charge layer increases as the distance to the sample surface decreases.

3.2. Time-resolved PL

The time-resolved PL profiles of the Na$_2$S-, Fc- and p-Me-NB-modified MQW samples are shown in Fig. 4. The decay times τ_{decay} of each profile were estimated by fitting the PL decays with a monoexponential function, i.e. $A\exp(-t/\tau_{\text{decay}})$, and are listed in Table 1. It can be seen that the PL decay time of each well is not influenced by molecular adsorption. However, the higher PL intensities of the Na$_2$S- and Fc-modified MQW samples relative to that of the blank sample are qualitatively consistent with the results of the steady state PL spectra.

These results indicate that the nature of the surface of the semiconductor can be changed considerably by the interaction of adsorbed molecules with the surface states, which play an important role in defining the electronic properties of the semiconductor interface. The surface interaction with adsorbed molecules alters the energetic distribution and electronic occupancy of the surface states, resulting in a corresponding change in the space charge layer. The thickness of

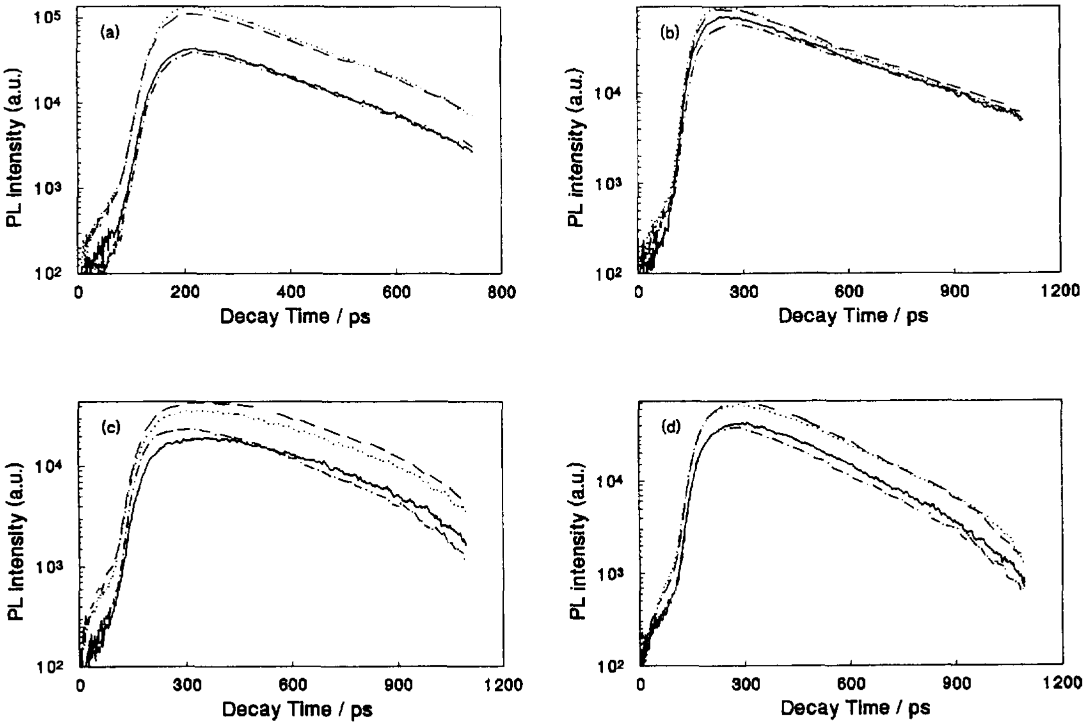

Fig. 4. PL decay curves of GaAs wells with different widths in GaAs/Al$_x$Ga$_{1-x}$As MQW structure modified with the following molecules: ———, blank; - · -, p-methyl-nitrobenzene; —, ferrocene; · · ·, Na$_2$S·9H$_2$O. Width of GaAs wells: (a) 1 nm; (b) 2 nm; (c) 8 nm; (d) 10 nm.

Table 1
PL decay time for modified GaAs/$Al_xGa_{1-x}As$ MQW

Well width (nm)	PL decay time τ (ps)			
	Blank	*p*-Me-NB	Fc	Na_2S
1	205	208	211	198
2	327	328	338	323
8	367	382	368	367
10	419	382	381	379

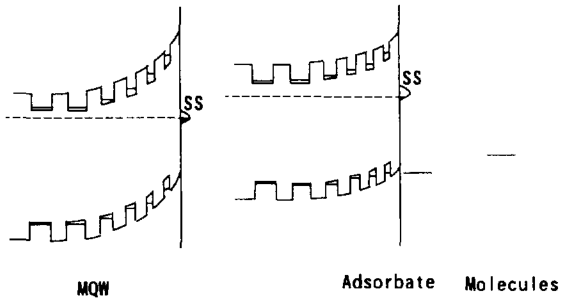

Fig. 5. Energy band scheme of MQW with adsorption of $Na_2S \cdot 9H_2O$, Fc or HQ molecules.

the space charge layer without illumination was estimated to be 1000 nm, and all the quantum wells are incorporated in the space charge layer. On the GaAs/$Al_xGa_{1-x}As$ MQW semiconductor surface with a thin naturally oxidized layer, anti-site arsenic As_{Ga} defects are the dominant surface states, represented as D^0/D^+ and D^+/D^{++} [16,17]. The interaction of the positively charged surface states with donor adsorbates (Na_2S, Fc [18] and HQ molecules) may increase the surface state energies up to the conduction band as shown in Fig. 5. This induces a width decrease and an electron density increase in the space charge layer, both of which are attributed to the increase in PL intensity due to the larger radiative recombination. The additional electron density in the space charge layer also enhances the carrier charge screening effect, leading to a red shift in the PL peak positions by reducing the energy level of the exciton [13,14,19]. The observed trend in the red shift of the PL peak positions depends on the magnitude of the interaction, correlating with the electron-donating ability of the adsorbates. In the case of *p*-Me-NB, which can be considered as an electron acceptor due to the electron-withdrawing character of the NO_2 substituent, interaction with the surface states may not change the features of the space charge layer. The photovoltage of MQW caused by illumination at 10 K is about ten times lower than that at room temperature [20,21]. Band bending of the space charge layer, induced by the photovoltage, can be neglected in this experiment. Therefore the red shifts of the PL emission peaks mainly arise from the interaction of the adsorbates with the surface states. The increase in the intensity of the emission peaks of the Na_2S- and Fc-modified MQW samples, shown in the PL decay spectra, analogous to that observed in the steady state PL spectra, is due to enhanced radiative recombination of the exciton in the corresponding wells. Since the Na_2S and Fc molecules adsorbed on the MQW surface cannot perturb the relaxation processes of the excitons that occur basically inside the wells at 10 K, the exciton decay time is virtually independent of molecular adsorption.

4. Conclusions

The surface interaction of the GaAs/$Al_xGa_{1-x}As$ MQW semiconductor with chemically adsorbed molecules of Na_2S, Fc, HQ and *p*-Me-NB was studied using the red shifts of the exciton emission peaks for a series of width-varying quantum wells located at different distances to the MQW surface. The magnitude of the red shift is distance dependent and follows the order, $Na_2S > Fc > HQ > p$-Me-NB, consistent with the electron-donating ability. The interaction of anti-site arsenic surface states with adsorbed molecules is suggested to be the dominant mechanism.

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