Photoluminescence Studies of Chemical Adsorption of GaAs/$Al_xGa_{1-x}As$ Multiquantum Well Semiconductor

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Adsorption of ferrocene and *p*-methylnitrobenzene on a GaAs/$Al_xGa_{1-x}As$ multiquantum well semiconductor is characterized by the changes in the photoluminescent response in terms of the interactions of adsorbed molecules with surface states.

The characteristics of semiconductor surfaces, which play important roles in the design of optoelectronic and photoelectrochemical devices, have attracted much attention for both fundamental and technological studies.[1–3] The properties of semiconductor surfaces can be modified by the chemisorption of a variety of organic or inorganic molecules. Many of these modifications improve the chemical and physical surface properties,[1,4,5] accompanying the electronic structural change induced by the interaction of semiconductor-adsorbed molecules, such as altering the distribution and occupancy of surface states (SS) and changing the electric field of the space charge layer (SCL). Photoluminescence (PL), as a sensitive technique capable of exploring molecular surface interactions, has been used to study the perturbation of the electronic structure of semiconductors by chemical adsorption.

Quantum well semiconductors can be used as a new kind of probe material to characterize the changes of electronic structure caused by chemisorption of molecules onto surfaces, owing to the spectral blue shifts arising from energy quantization and the confinement energy of excitons altered by the electric field, and the carrier screening effect of the SCL. More information on surface interactions with adsorbed molecules can be readily obtained in molecule-modified quantum well semiconductor systems. In this communication, lattice-matched multiquantum well (MQW) GaAs/$Al_xGa_{1-x}As$ crystals with wells of various thicknesses have been designed and prepared for PL studies of chemical adsorption.

The lattice-matched GaAs/$Al_{0.35}Ga_{0.65}As$ MQW crystal consisting of GaAs well and $Al_{0.35}Ga_{0.65}As$ barrier ultrathin alternating layers were grown on an n^+-GaAs(100) (1×10^{18} cm^{-3}) substrate by molecular beam epitaxy (MBE). The structure of the MQW crystal studied here is as follows: unintentionally doped epitaxial layers, including a 200 nm thick GaAs buffer layer, a 500 nm thick $Al_{0.35}Ga_{0.65}As$ inner barrier, 11 quantum well layers with sequential thicknesses of 60, 50, 40, 30, 20, 10, 8, 6, 4, 2 and 1 nm, and a 20 nm $Al_{0.35}Ga_{0.65}As$ outer barrier, and finally a 20 nm GaAs capped layer. The quantum wells were each separated by 20 nm thick $Al_{0.35}Ga_{0.65}As$ barrier layers. Before surface adsorption of molecules, the MQW crystal samples were successively ultrasonicated in alcohol, acetone and acetonitrile. Ferrocene (Fc) and *p*-methylnitrobenzene (*p*-MeNB) as organic adsorbates were dissolved in acetonitrile and transferred onto a clean surface of the MQW sample by a dropping method. The amount of covered molecules on the sample surface was estimated to be 10^{-6} mol cm^{-2}. The photoluminescence spectra were recorded at an excited wavelength of 632.8 nm from a He–Ne laser with light intensity of 2 W cm^{-2} at a temperature of 10 K.

The PL spectra of the MQW specimens show 8 sharp emission peaks as solid lines in Fig. 1(*a*) and (*b*) at the 1.519, 1.529, 1.557, 1.576, 1.607, 1.665, 1.785 and 1.877 eV positions, which were produced by GaAs bulk and 20, 10, 8, 6, 4, 2 and 1 nm width GaAs quantum wells, respectively, owing to quantum confinement effects. The emission peaks of the quantum wells wider than 20 nm overlapped with the peak of the GaAs bulk at 816.5 nm. These peaks correspond to the recombination transitions between an electron and a heavy hole in the lowest eigenstates of each well. After adsorption of Fc and *p*-MeNB, the PL spectra of the MQWs are shown as dashed lines in Fig. 1(*a*) and (*b*), respectively. Red shifts in PL peak positions and dramatic increases of intensities are apparent in the PL spectra of Fc-modified MQW samples. Comparing the displacement of the peak energy of each well with its distance to the MQW surface, we find that Fc adsorption-induced peak energy displacements occurred at the near surface wells and their behaviour is distance dependent. Peak energy displacements as a function of well-to-surface distances are illustrated in Fig. 2. Energy displacements increase remarkably with the reduction of well-to-surface distance, indicating that the characteristics of the SCL are influenced directly by the surface interactions with adsorbed Fc molecules, which are stronger near to the surface. Contrary to Fc adsorption, Fig. 1(*b*) shows no obvious changes of PL peaks in either positions or intensities in the PL spectra of *p*-MeNB-modified MQW samples. These phenomena reveal that the surface behaviour of MQW is insensitive to the adsorption of *p*-MeNB molecules.

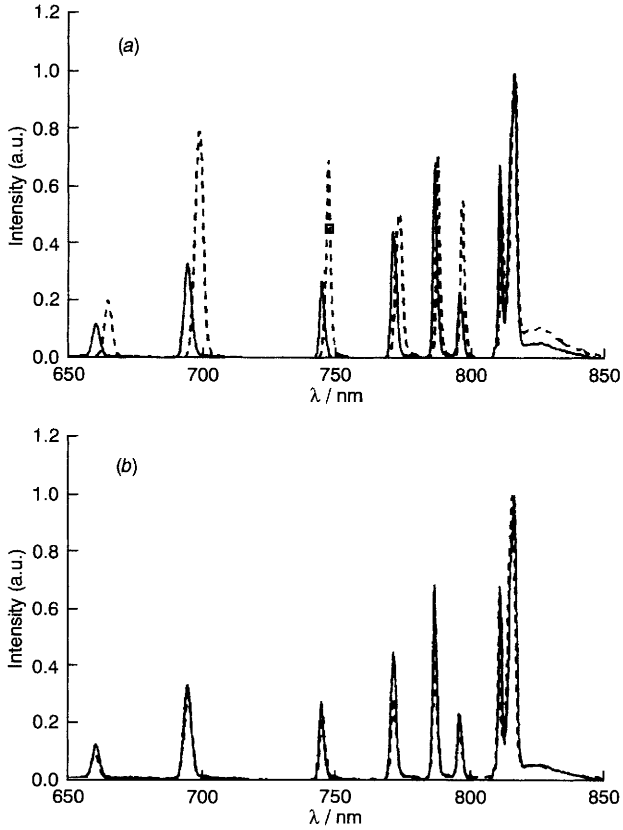

Fig. 1 The photoluminescent spectra of GaAs/$Al_xGa_{1-x}As$ multiquantum well semiconductors modified by organic molecules: (*a*) —— blank; — — after adsorption of ferrocene, (*b*) —— blank; — — after adsorption of *p*-methylnitrobenzene

The quite different effects of molecular adsorption on the PL changes can be explained briefly as follows. The nature of the surface states, such as energetic distribution and electronic occupancy, which are very important in defining the electronic properties of semiconductor interfaces, is altered considerably by surface adsorption, leading to corresponding changes in the SCL. The thickness of the SCL on the surface without illumination was estimated to be 1000 nm, and all the quantum wells are incorporated in the SCL. After Fc adsorption, ferrocene as a donor[6] adsorbate can interact with GaAs surface states which are considered to be acceptor species,[7] raising surface state energies closer to the conduction band-edge, as shown in Fig. 3, and resulting in a decrease in band bending and an increase in the electron density in the SCL.[1] Therefore, the PL intensities are enhanced because of the increase of radiative recombination. The additional electron density in the SCL enhances the carrier-charge screening effect, leading to a reduction of the engery level of the exciton[8] and accompanied by the red shift of the PL peak positions. The photovoltages of MQW caused by illumination at 10 K, are much lower than at room temperature. Band bending of the SCL induced by photovoltages can be neglected in this experiment. Therefore, the observed red shifts of PL emission peaks in the PL spectra of Fc-modified MQW mainly arise from the changed band-bending induced by the interaction of surface states with the Fc adsorbate. The p-MeNB with electron-withdrawing substituents acted as acceptor adsorbate cannot produce a corresponding change in the SCL by interaction with surface states. Further studies of molecular adsorption onto MQW are currently in progress.

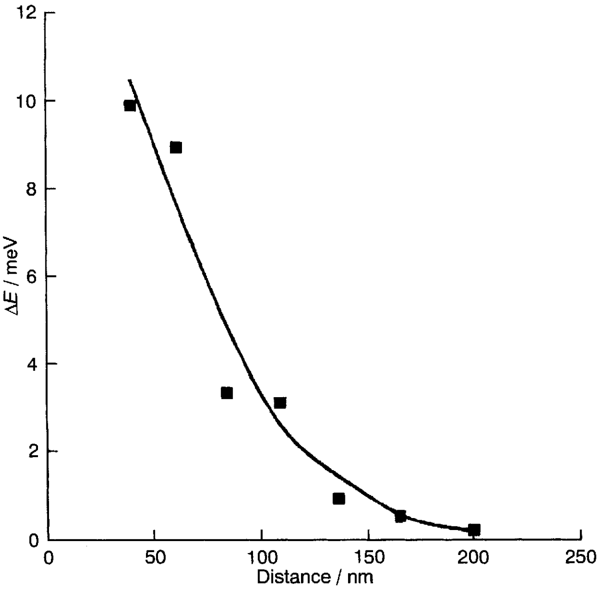

Fig. 2 Dependence of the displacements of exciton energy level on the distance from the quantum well to the surface for ferrocene-adsorbed MQW samples

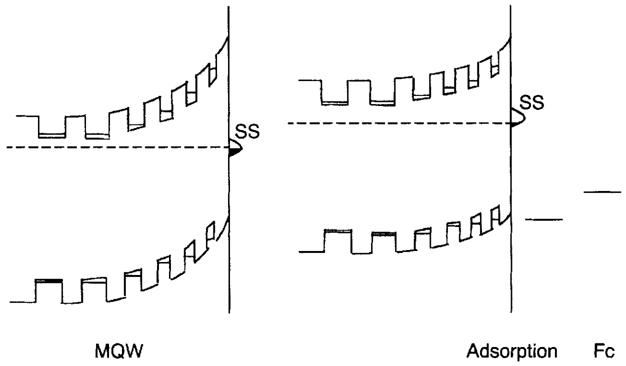

Fig. 3 Energy-band scheme of MQW with adsorption of ferrocene

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